CHARGE CHARACTERISTICS OF SELECTED SOILS FROM TROPICAL AREAS

By

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To my Father,

Melitón Adams,

who died May 1978

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Ten soils from Venezuela and one from Florida, U.S.A., were investigated by chemical, physical, and mineralogical techniques to elucidate surface reactivity. Also, two Oxisols and one Alfisol were selected to determine the effect of lime and P levels on surface charge. A sorghum crop was planted under greenhouse conditions to investigate the change of surface charge in each lime- and P-treated soil after cropping. Stern and Gouy-Chapman models for diffuse double layer together with the point of zero net charge (PZNC) and the surface area were used to calculate the charge distribution and the cation exchange capacity (CEC) of the soils for each lime and P treatment.

The following parameters were determined: (a) acidity sources; (b) quantity-intensity K relationships; (c) P fractionation in virgin soils and after P adsorption; (d) P-adsorption isotherms at different temperatures and with different ionic systems; (e) PZNC of virgin soils before and after lime and P treatments; (f) pH before and after cropping; (g) electrical conductivity before cropping; and (h) sorghum dry-matter yields.

The following parameters were calculated: (a) thermodynamic parameters associated with the adsorption process ($\Delta G°$, $\Delta H°$, and $\Delta S°$) and (b) charge distribution in double layer and CEC after lime and P treatments.

The results showed that exchangeable Al^{+3} and dissociation of OH groups from organic matter and silicate are responsible for the acidity in these soils. The soils had low available K, but very high selectivity for K. There was an increase in P adsorption with temperature in all soils. Lime increased P adsorption in two Alfisols and one Oxisol. There was an increase in both Al-P and Fe-P with temperature and P concentration applied. Phosphorus had a highly significant effect on PZNC decrease while P and lime increased CEC due to the combined decrease of PZNC and increased pH. Salt content as indicated by increasing electrical conductivity may have depressed the dry matter yield of sorghum in lime and P treatments. The negative $\Delta G°$ values and positive values of $\Delta H°$ and $\Delta S°$ showed that P adsorption in these soils is a spontaneous endothermic reaction that occurs with an increase of entropy resulting from displacement of water molecules by phosphate ions.

INTRODUCTION

Physico-chemical properties of a soil are determined by the surface characteristics of its organic and inorganic colloidal components. The quantity and type of those components are greatly affected by various soil-forming environmental conditions. Because of the great variations in climate, topography, etc., soils in Venezuela vary from relatively recently formed Entisols and Inceptisols to highly weathered Ultisols and Oxisols. Like other tropical regions, highly weathered soils dominate in Venezuela. These soils are mostly acidic and P deficient. Finding ways of making tropical soils more productive, by correcting soil acidity and making conditions favorable for nutrient retention and uptake by crops are the concern of most soil research in tropical countries. A study of surface phenomena such as proton release, cation selectivity, P adsorption, and the effect of liming and P application on surface charge can help our understanding of the behavior of highly weathered tropical soils with concomitant implications to their management. Of particular significance is the efficient use of P in soils because farmers wish to manage their chemical investment in the most economical manner and this element is one of the most expensive. The phenomenon of P adsorption directly influences the magnitude of available P for crops in highly weathered soils.

The intent and objectives of the study presented herein were to elucidate (a) sources of acidity, (b) ion selectivity, (c) adsorption

and release of P, and (d) effects of $CaCO_3$ and P treatments on surface charge (CEC) as related to crop production in selected soils from Venezuela.

LITERATURE REVIEW

Evaluation of soils in relation to classification, agronomic practices, and other purposes is aided by the identification, characterization, and understanding of their properties and behaviors. Soil surface reactions involving source of protons, ionic selectivity, specific adsorption, and responses to chemical treatments have great importance in the understanding of electrochemical behaviors of highly weathered soils.

Soil Characteristics

Mineralogical Characteristics

Physical and chemical properties of any soil are controlled to a very large degree by the minerals in the soil and especially by those constituting the clay fraction. Identification, characterization, and an understanding of properties of the different minerals aid in the evaluation of soils in relation to classification, agronomic practices, and other purposes. Positive identification of mineral species and quantitative estimation of their properties in the soil clay fraction usually require the application of several qualitative and quantitative analyses. X-rays diffraction, CEC, and surface area are among the most common analytical measurements used by soil scientists (Jackson, 1956; Whittig, 1965).

Some soil constituents interfere in the soil mineralogical analysis. In these cases, a chemical pretreatment of the soil is necesary.

Pretreatments are designed to have a minimum effect on fractions of the soil other than those for which the treatments are intended. The pretreatments that are most used in soil mineralogical analyses are removal of salts, carbonates, Fe, organic matter and amorphous material, and particle-size fractionation (Jackson, 1956).

Soluble salts and carbonates affect organic matter removal, soil sample dispersion, and also make it impossible to saturate the exchange complex with a specific cation. Removal of soluble salts and carbonates simplifies X-ray diffraction analysis. Carbonates reduce degree of orientation of particles in slide preparation (Jackson, 1956).

Organic and Fe-oxide cementing agents are frequently removed by chemical treatment prior to clay separation to obtain dispersion for effective particle-size separation, enhanced parallel orientation of clays, and decreased background and attenuation of X-rays (Zelazny and Carlisle, 1971).

Mehra and Jackson (1960) found that citrate system was the most effective in removal of free Fe-oxides from latosolic soils and the least destructive of Fe-silicate clays as indicated by least loss in CEC after Fe-oxide removal.

On the other hand, organic matter may cause a high background and prevent parallel orientation in the preparation of the slides for X-ray diffraction studies. Traditionally, organic matter has been oxidized with H_2O_2. In order to prevent a strong acid condition from developing which could degrade crystalline minerals, soils have to be buffered around pH 5 in the presence of H_2O_2.

Mineralogical analyses are normally performed on specific size fractions of the soil such as 2 to 0.2 microns. For mineralogical study, concentration of the clay fraction is necessary (Jackson, 1956).

Identification and quantitative analysis of the minerals are possible from an X-ray diffraction pattern because each diffraction peak depends upon the atomic arrangement in the crystal and is proportional to the concentration of the mineral in a mixture (Jackson, 1956). The choice of cations for saturation of the exchange sites along with solvation becomes important especially since spacings of expanding clay minerals are made larger with Mg and Ca ions than with K or Na ions (Jackson, 1956).

Soil Acidity Sources

In most of the soil classification studies and in soil characterization for agricultural purposes, the pH value has great importance. Deficiencies of P, Ca, Mg and Mo, and Al and Mn toxicities seem to be the most important effects of soil acidity on plant growth (Lora and Riveros, 1971).

Soil acidity has been defined as a soil system's proton yielding capacity in going from a given state to a reference state. Soil acidity has long been recognized to involve exchangeable Al (Jackson, 1963). Acid soil systems that are Al-saturated have weak acid characteristics while those that are H-saturated have strong acid characteristcs (Coulter, 1969). But the latter is an unstable state because H ions attack the clay structure and Al is released as shown by Davis et al. (1962) in their study of autotransformation of H-bentonite to Al-bentonite.

On the other hand, Yuan (1963) studied H and Al ions, and pH relationships in pure chemical solutions and compared the results with those obtained from several soil systems. He pointed out that pH determined with the usual methods can be considered as a measure of the H ion

activity in the system when the liquid and solid phases are in equilibrium. He also indicated that soils with the same H ion activity and different amounts of unhydrolyzed Al ions may have the same pH.

Since Bradfield (1941) pointed out the nature of potentiometric and conductometric titrations in soil systems, these techniques have been very useful in studying the nature of soil acidity. Several authors have studied the factors that affect the results obtained with these techniques. Low (1955) pointed out that potentiometric and conductometric titrations could be used to determine the amount of Al on an acid bentonite. On the other hand, Marshall (1964) showed initial inflections due to H titration, followed by regions of buffering attributable to Al. These inflections and their corresponding indication of soil acidity sources can be verified by bases that titrate specifically H or Al. Yuan (1959) used fluoride to eliminate the interference of Al ions in the H titration.

It was found that $Na_2B_4O_7$ titrations gave the permanent negative charge on montmorillonite particles both when this clay contained exchangeable Al and when it did not (Shainberg and Dawson, 1967). They also pointed out that the differences between NaOH and $Na_2B_4O_7$ titrations can be made equivalent to H ions formed from proton release by hydroxyl groups, and by selecting an appropriate end point, it can be made approximately equal to this quantity plus the aluminate equivalent of exchangeable Al. They also determined the effect of salt content on the slope of the first segment of the conductometric curves.

Chao and Harward (1962) found that the features of titration curves were independent of the kind of clay and dependent on the nature of the acid clay. Rich (1970) pointed out that the differences in results of

both potentiometric and conductometric titrations, and of extractions by neutral salts of acidity from $AlCl_3$- treated cation exchangers were due to the fact that neutral salts, especially K salts, tend to induce hydrolysis of Al^{+3} ions on exchange sites. Dewan and Rich (1970) found that consistent results are obtained when the aluminate reaction is considered for titrations with strong bases.

Lime Requirement

The several methods that have been proposed to determine lime requirement of acid soils have advantages and disadvantages depending on type of soil and intended use of the data. However, it is now generally accepted that the most reliable index for predicting lime requirement of soils of tropical regions is the quantity of exchangeable Al (Reeve and Sumner, 1970a; Kamprath, 1970; Evans and Kamprath, 1970; Amedee and Peech, 1976). However, the incubation method still appears to be as good as any, if the desired pH level is not as high as complete neturalization. Spain et al. (1975) pointed out that liming rates for soils of the tropics often have been overestimated even when based on Al suppression. Pearson (1975) concluded that relatively low rates of lime in the humid tropics are usually adequate for maximum crop production.

Potassium Quantity/Intensity Measures

Because of the importance of K in plant nutrition, many investigators have attempted to find a rapid and reliable method for evaluation of K availability in soils. Potassium availability depends on the exchangeable form of this element in the double layer surrounding the exchange complex. The chemical potential of K in the double layer controls the activity of K in solution (Beckett, 1964a). Its chemical potential cannot be measured experimentally and is not directly

proportional to the activity of K in the soil solution (San Valentin et al., 1972). Beckett (1964b) proposed the activity ratio $aK/(aCa + Mg)^{\frac{1}{2}}$ as a measure of the ruling chemical potential of labile K in a soil. The activity ratio, which is now stated as AR^k, has the same value for all solutions in equilibrium with a given soil, and is independent of the ionic strength of the soil solution or the proportion of Ca to Mg (Beckett and Nafady, 1967b). This ratio is related to availability of K and is termed intensity (I) (Beckett, 1964b). The ability of a soil to maintain the activity ratio against depletion by plant roots is governed by the character of the pool of labile K, the rate of release of fixed K, and the diffusion and transport of K ion in the solution (Beckett, 1964c). The relationship between K availability or intensity (I) and the amount of K present (Q) in soils is termed the Q/I relationship (Beckett, 1964a).

The Q/I relationship can be determined by equilibrating a sample of soil with solutions containing a constant amount of $CaCl_2$ and increasing amounts of KCl. The soil either gains or losses K in order to achieve the characteristic AR^k of that soil, or remains unchanged if its AR^k is the same as that of the equilibrating solution. The characteristic Q/I relationship is formed by plotting the gain or losses of K (ΔK) against the AR^k of the equilibrium solution (San Valentin et al., 1972; Beckett and Nafady, 1967a, 1967b). San Valentin et al. (1972) pointed out that three parameters are derived from a Q/I plot which can characterize the soil K status. When $\Delta K=0$, the AR^k is a measure of the K availability at equilibrium (termed ΔR^k_e). When $AR^k=0$, the value of K is a measure of the labile or exchangeable K in soils (termed $\Delta K°$). The slope of the linear portion of the curve gives the Potential Buffering Capacity of the soil for K (termed PBC^k) and is proportional to CEC.

The curved portion of the Q/I plot is also an indication of the number of specific sites for K. The number of specific sites for K (termed K_x) is determined from the difference between the intercept of the curved and linear portions of Q/I plot at $AR^k=0$.

Forms of the Q/I relationship remain almost unchanged either by large K additions, a high degree of K fixation, or by depletion of labile and some fixed soil K. However, acidic M $CaCl_2$ solutions may influence the form of Q/I relationship by removing substances blocking portions of the exchange surfaces of the soil clay, increasing the extent of the exchange surface participating in the Q/I exchange equilibria, inducing the collapse of the expanded portion of soil clay, and by decreasing the extent of those exchange surfaces (Lee, 1973).

Moss and Beckett (1971) reviewed the sources of error in the determination of soil K activity ratios by the Q/I procedure. They pointed out that errors may arise in sampling, preparation and storage of soil samples, and recommended analysis of samples as soon as possible after sampling, with only gentle sieving. They also found that exchange between cations and soluble salts or microbially dissolved carbonates during the determination affect the results obtained by this procedure.

Phosphorus Fractions

Knowledge of specific chemical forms of phosphates is important in understanding the chemistry of soil P and also has importance in soil genesis and soil fertility. In acid soils, P forms insoluble compounds with Fe and Al while under alkaline conditions, Ca compounds are formed. The particular compounds formed depend on soil properties. Furthermore, the solubility and stability of these compounds affect the availability of P under field conditions.

Juo and Ellis (1968) showed that when soluble P is applied to acid soils, or when Ca-P is dissolved during the process of chemical weathering, the soluble P precipitates rapidly to form colloidal Al-P and Fe-P. The P in these colloidal forms is relatively available to plants initially, but crystallization tends to form hydrated compounds such as variscite and strengite that are less available. Furthermore, Fe-P crystallizes at a more rapid rate than Al-P and this is why Al-P seems to be more available to plants than Fe-P. Singh et al. (1966) studying the availability of forms of residual P in Davidson clay loam found that neutral soils, pH 6.8, favored the availability of Al-P to first-cutting alfalfa and Fe-P to first-, second-, and third-cutting alfalfa. They also pointed out that Al and Fe activities at this pH are low, and as a result, P from Al- and Fe-P becomes more available to plants. Lindsay and Moreno (1960) pointed out that in soil below pH 7, the $H_2PO_4^-$ constitutes the larger fraction of the total P in solution and the logarithmic acitivity function permits a linear relationship with pH. They developed a phase diagram that permits prediction of the $H_2PO_4^-$ concentration as controlled by variscite, strengite, fluorapatite, hydroxyapatite, octocalcium phosphate, and dicalcium phosphate solubilities. In that diagram, increase in pH tends to decrease precipitation of Al and Fe compounds, but increase precipitation of Ca forms.

Yuan et al. (1960) studying newly fixed P forms in acid sandy soils found that the ratio Al-P to Fe-P increased with increasing rates of applied P. They also found that increasing soil drying temperature decreased the percentage of P in Al-P form, but increased that in Fe-P form. Fractionation of inorganic soil phosphates is widely used in soil fertility and genesis studies. These procedures are based on

differential solubilities of inorganic phosphates in various extractants. The most used of these methods is that of Chang and Jackson (1957) modified by Petersen and Corey (1969); these procedures differ only in the sequence of extraction of the different P forms, pH of the NH_4F solution used to extract Al-P which reduces interference by Fe, and other details to increase the efficiency of analysis of a large number of samples.

Phosphorus Adsorption

Adsorption is the process of concentration of liquid or gaseous material on the surface of a solid. Phosphorus adsorption studies may be divided into those concerned with investigating the nature and mechanism of the sorption system, and those concerned with its quantitative measurement (Larsen, 1967).

Measurement of the size of the P adsorption system can be made by fitting adsorption data to a previously described adsorption isotherm. The Langmuir isotherm has often been used for this purpose.

The Langmuir isotherm has constants which, at least when applied to the adsorption of gases on solids, have quantitative meaning. The linear form of the Langmuir isotherm is

$$\frac{c}{x/m} = \frac{1}{Kb} + \frac{c}{b}, \qquad (1)$$

where $\frac{x}{m}$ = mg P adsorbed/100g soil

b = the adsorption maximum, mg/100g soil

c = equilibrium P concentration, moles/liter

k = a constant related to the energy of bonding.

The Freundlich isotherm has the form

$$x = ac^b \qquad (2)$$

or the linear form

$$\log x = \log a + b \log c, \qquad (3)$$

where x is the amount of P adsorbed per unit weight of soil, c is the concentration of P in solution, and a and b are the constants that vary between soils. Larsen (1967) claimed that this isotherm is purely empirical, and the constants have no physical meaning. However, Adamson (1976) pointed out that the Freundlich equation, unlike the Langmuir, does not become linear at low P concentration but remains convex to the concentration axis. Also, it does not show a saturation or limiting value, but the intercept of log x vs log c gives a measure of the adsorbent capacity and the slope of adsorption intensity.

Factors affecting adsorption equilibrium. Equilibrium adsorption of P studies on a variety of soils and minerals have shown that several factors have consistent influence on the final position of the equilibrium state. Among these factors are (a) concentration of P in the solution, (b) temperature, (c) ionic strength, (d) the pH, and (e) specific cation interactions with the surface and adsorbed species. Noting the apparent independence of the adsorption isotherm from the overall adsorption capacity of the adsorbent material, Muljadi et al. (1966) proposed employing an empirical splitting of the isotherms into three regions. The regions, designated I, II, and III, were found to correspond to equilibrium solution concentration ranges which may be described roughly as low, medium, and high, respectively. Regions I and II fit a Langmuir adsorption isotherm while region III exhibited a linear dependence on solution concentration. They also found that adsorption in regions I and II increased irreversibly with increasing temperature, while the increase in region III was reversible with respect to temperature. Ryden

et al. (1977) later employed this curve splitting technique and reported on the effects of pH, ionic strength, specific cation, and cation adsorption. These authors noted that Ca electrolyte solutions were more effective in facilitating adsorption than Na solutions of the same ionic strength; in conjunction with this finding, the authors reported observing a specific adsorption of Ca which was not reversible to 1N KCl. Sodium adsorption was measured together with phosphate adsorption and it was observed that the adsorption of Na corresponded to that of phosphate in regions I and III, but that no Na was adsorbed in region II. They interpreted those results in terms of the adsorption mechanisms in the three regions. Region I was thought to represent the replacement of adsorbed water by phosphate; region II, the displacement of surface hydroxyls; and region III, the association of phosphate ligand with the surface metal which was potentially dependent and less energetic than a specific electrovalent coordination with the metal. The concentration of phosphate in solution was thought to affect both the amount of P adsorbed and the nature of the adsorption process.

Temperature effects on equilibrium adsorption isotherms have been reported for soils and minerals. Muljadi et al. (1966) measured phosphate adsorption on K-kaolinite, gibbsite, and pseudoboehmite at 2, 20, and 40°C, respectively. They reported a marked increase in adsorption with temperature for the three equilibrium concentration regions. Region I of K-kaolinite (pH 5) reached a maximum at about 20°C; regions II and III showed increases to 40°C for all adsorbents. The increase in adsorption in region I was reported to be irreversible with respect

to temperature; region II was slightly reversible for K-kaolinite but irreversible for gibbsite and pseudoboehmite; and region III was found to be completely reversible. Barrow and Shaw (1975a) measured the adsorption of phosphate on soils as a function of time and temperature. They observed an increase in adsorption with temperature from 4 to 42°C for contact times up to 100 days. However, they reported that adsorption exhibited a time-temperature dependence which indicated that increasing temperature merely speeded up the adsorption process, rather than shifting the equilibrium position.

Griffin and Jurinak (1974), studying the kinetics of interaction of phosphate with calcite at 0, 11, 23, and 40°C, demonstrated that temperature has a much more pronounced effect on the adsorption rate constant than on the desorption rate constant. These results indicated that the adsorption process is favored by an increase in temperature and that equilibrium adsorption should increase over the temperature range studied.

The effects of the ionic strength and of selected cations on the adsorption of phosphate have been reported for a group of Hawaiian soils (Ryden et al., 1977a, b) and gibbsite (Helyar et al., 1976a). Ryden and coworkers, observing a linear relationship in plots of the solution phosphate concentration against the reciprocal of time for periods greater than 72 hours, were able to estimate the equilibrium concentration for a series of solutions of differing ionic strengths. The plots converged at equilibrium for low phosphate concentrations, indicating that the ionic strength effect was kinetic. At moderate to high solution concentrations, the ionic-strength effect was found to be absolute and the authors concluded that the adsorption at high

solution concentrations was potentially determined. Adsorption from solutions with a $CaCl_2$ - supporting electrolyte was greater than from NaCl solutions; however, the pH of the Ca solutions was lower. The authors, noting that more Ca was adsorbed than Na and that the adsorbed Ca was not completely displaced by 1N KCl, proposed that Ca was specifically adsorbed, thus facilitating the adsorption of phosphate. Helyar et al. (1976a) studied the effect of selected cations on the adsorption of phosphate on gibbsite. They maintained a constant pH by controlling the partial pressure of CO_2 in the solid-solution mixture. Their results for Na, K, and Mg were similar and the observed ionic strength effect was small. Adsorption in the presence of Ca, however, increased out of all proportion to the change in ionic strength for equilibrium concentrations above 1.0 μM, but converged with the adsorption noted for other cations at lower equilibrium concentrations.

Helyar et al. (1976b) proposed that certain cations could facilitate adsorption by forming a stabilizing bridge between two adsorbed phosphate ligands. The ability of the cation to form such a bridge would depend upon its fit into the space between the oxygen of two adjacent phosphates and its ability to coordinate with two oxy-ligands. The authors estimated an oxygen to oxygen distance of approximately 1.0 Å for adsorption on gibbsite; cations of approximately this crystal radius and divalent charge would best accommodate the space if they could form coordinate covalent bonds. They selected a number of cations with a range of radii for both mono and divalent species. The adsorption of phosphate was enhanced markedly by Ca, Cd, and Sr which have radii of 0.99, 0.99, and 1.13 Å, respectively. No such enhancement was noted for Mg, Zn, Na, or K which have radii of 0.66, 0.74, 0.95, and 1.37 Å,

respectively. The stabilizing effect of a bridging cation was thought to result from a reduction of the mutual repulsion of the oxygen or hydroxyl groups on adjacent phosphate ligands.

Thermodynamic parameters associated with adsorption process. Thermodynamic parameters calculated from adsorption measurements have been found useful in elucidating the mechanisms involved (Biggar and Cheung, 1973). Biggar and Cheung (1973) calculated the thermodynamic parameters associated with the adsorption process from the variation of the thermodynamic equilibrium constant, Ko, with changes in temperature. Ko for the adsorption reaction is defined as:

$$Ko = \frac{as}{ae} = \frac{\gamma s \; Cs}{\gamma e \; Ce} \qquad (4)$$

where as = activity of the adsorbed solute, ae = activity of the solute in the equilibrium solution, Cs = μg of solute adsorbed/ml of solvent in contact with the adsorbent surface, Ce = μg of solute/ml of solvent in the equilibrium solution, γs = activity coefficient of the adsorbed solute, and γe = activity coefficient of the solute in the equilibrium solution.

Cs is calculated according to the following equation:

$$Cs = \frac{(\rho_1/M_1)\; A_1}{\frac{S}{Na\;(x/m)} - \frac{A_2}{M_2 \times 10^6}} \qquad (5)$$

where ρ_1 = density of solvent (g/ml); M_1 and M_2 = molecular weights (g/mole) of the solvent and the solute, respectively; A_1 and A_2 = cross-sectional areas (cm^2/molecule) of the solvent molecule and the solute molecule, respectively; Na = Avogadro's number (6.02×10^{23} molecules/mole); S = surface area of the adsorbent (cm^2/g); and x/m = specific adsorption (μg/g).

The cross-sectional areas (in cm^2) of the solvent and solute molecules were estimated from the following equation:

$$A = 1.091 \times 10^{-16} \left[\frac{M \times 10^{24}}{Na\rho} \right]^{2/3} \qquad (6)$$

where M and ρ are, respectively, the molecular weight (g/mole) and the density (g/ml) of the solvent or solute. Biggar and Cheung (1973) assumed that

$$\frac{S}{Na\ (x/m)} >> \frac{A_2}{M_2 \times 10^6} \qquad (7)$$

and reduced equation (5) to

$$Cs = \frac{(\rho_1/M_1) \times A_1}{\frac{S}{Na\ (x/m)}} \qquad (8)$$

and calculated Cs from this equation. They also assumed that concentration of the solute in the solution approaches zero, and γs and γe approach unity. The authors obtained the values of Ko by plotting ln (Cs/Ce) vs Cs and extrapolating to zero Cs. The standard free energy, $\Delta G°$, was calculated from

$$\Delta G° = - RT \ln Ko. \qquad (9)$$

The standard enthalpy, $H°$, is obtained from the integrated form of the van't Hoff equation,

$$\ln \frac{Ko2}{Ko1} = - \frac{\Delta H°}{R} \left(\frac{1}{T2} - \frac{1}{T1} \right). \qquad (10)$$

The standard entropy, $\Delta S°$, is obtained from

$$\Delta S° = (\Delta H° - \Delta G°)/T. \qquad (11)$$

Biggar and Cheung (1973), noting the linear nature of ln Ko vs 1/T, concluded that the mechanics of adsorption were not changed as temperature was changed and that the amount of adsorption was changed because the supply of thermal energy was different.

Rydens et al. (1977) used the expression:

$$G = - RT \ln K \qquad (12)$$

where K is the Langmuir equilibrium constant obtained for a single temperature and has units of reciprocal concentration. Assuming that K exhibits a temperature dependency, the value of the estimated ΔG will depend upon the measurement temperature of K, and the concentration units used.

Some parameters related to the adsorbent capacity and the intensity of adsorption could be calculated using the Freundlich equation. In a plot of ln X vs log c where X = P adsorbed (µg/g), and c the equilibrium concentration (moles/liter), the intercept gives lnK that can be used to determine a ΔG related to the adsorption capacity energy (Adamson, 1976).

Using Ryden et al. (1977a, b) plots of the solution phosphate concentration vs the reciprocal of time to determine the equilibrium concentration by extrapolating at infinite time, an equilibrium constant can be calculated:

$$Keq = \frac{[Soil\text{-}P]}{[PO_4][Soil]} \qquad (13)$$

where [soil-P] is µg of P adsorbed per g of soil, $[PO_4]$ is equilibrium concentration in µg/ml, and [soil] is g of soil/liter of solution. Applying (12), a ΔG for adsorption can be calculated.

Surface Charge

Double-layer Models

Soil electrochemical behavior is determined by the quantity, type, and interactions of colloidal components. Colloids with a constant surface potential have a reversible double layer with the surface charge determined by the nature of the potential-determining ions (PDI) adsorbed on the surface. The electrical double layer at the solid-solution interface is constituted by the surface charge and its countercharge in solution. Solid oxide particles immersed in aqueous electrolyte solution develop surface electrical charges by adsorption or desorption of potential-determining ions (Atkinson et al., 1967). For oxides, the surface charge and surface potential are functions of solution pH, and H^+ and OH^- are referred to as potential-determining ions (Breeuwsma, 1973). The electrochemical behaviors of Oxisols and Alfisols were found to be similar to those exhibited by many metallic oxides (Van Raij and Peech, 1972).

The constant-potential surfaces are associated with oxides and hydroxides of metals and edges of clay minerals as well as with those clay minerals with minimal ion substitution in the lattice (Tinsley, 1974). These colloids include crystalline and noncrystalline oxides and hydrous oxides of Al, Fe, Ti, Mn, and Si; kaolinite, halloysite; allophane; quartz; and organic matter. The surface potential remains constant, and its magnitude is not affected by the presence of indifferent electrolytes (Stumm and Morgan, 1970).

For constant-potential surfaces, the surface charge is directly related to the concentration of potential-determining ions in the solution. The surface charge density of minerals of this type varies with pH and salt concentration (Keng and Uehara, 1974). From known surface

areas and Point of Zero Net Charge (PZNC) determination of Oxisols, the values for net electrical charge calculated by the application of Gouy-Chapman and Stern models of the double-layer theory were found to be in good agreement with experimental results (Van Raij and Peech, 1972; Adams, 1976).

Gouy-Chapman double-layer model. The Gouy-Chapman model relates the charge density of the surface with the surface potential as follows:

$$\sigma = (2n\varepsilon KT/\pi)^{\frac{1}{2}} \operatorname{Sinh} (Ze\psi o/2KT) \qquad (14)$$

where σ = the surface charge density

n = the concentration of the equilibrium solutions in number of ions per cm^3

ε = the dielectric constant of the medium

e = the charge of an electron

K = the Boltzmann constant

T = the absolute temperature

Z = the valence of the ion

ψo = the surface potential.

In constant-potential systems, change in concentration will result in a change in surface-charge density (σ). For some constant-surface potential colloids, ψo can be held constant by maintaining the pH constant (Keng and Uehara, 1974).

The Nernst equation can be used to relate the H^+ ion concentration to the surface potential as follows:

$$\psi o = \frac{RT}{ZF} \ln \frac{H+}{H^+_o} \qquad (15)$$

where R = the gas constant

F = the Faraday constant

H^+ = the hydrogen ion concentration

H_o^+ = the hydrogen ion concentration at which $\psi o = o$.

At 25°C the Nernst equation can be reduced to the following:

$$\psi o = 59(PZNC - pH) \qquad (16)$$

where PZNC is the pH at the point of zero net charge (pHo).

The Gouy-Chapman model for the double layer has limited quantitative application because of the assumption that ions in solution behave as point charges and can approach the surface without limitation (Tinsley, 1974).

Stern double-layer model. In the Stern double-layer model, charge density can be described by the following equation (Van Raij and Peech, 1972):

$$\sigma = \sigma_1 + \sigma_2$$

where σ_1 = Stern layer charge

σ_2 = diffuse layer charge.

The Stern layer charge can be given by

$$\sigma_1 = \frac{N_1 Ze}{1 + (Na\rho/Mn)\exp\left[\frac{-2e\psi\delta + \phi}{KT}\right]} \qquad (17)$$

where N_1 = available spots per cm^2 for adsorption of ions

Na = Avogadro's number

M = molecular weight of the solvent

ρ = solvent density

$\psi\delta$ = electrical potential at the boundary between the Stern layer and the diffuse layer or the Stern potential

ϕ = specific adsorption potential.

The diffuse-layer charge is given by the following equation:

$$\sigma_2 = (2n\epsilon KT/\pi)^{\frac{1}{2}} \text{ Sinh } (Ze\psi\delta/2KT) \qquad (18)$$

Since a linear drop in potential across the specific Stern layer is assumed, the surface charge can also be given by the Gauss equation for a molecular condensor:

$$\delta = \frac{\epsilon^1}{4\pi\delta} (\psi o - \psi\delta) \qquad (19)$$

where ϵ^1 = average dielectric constant

δ = average thickness of double layer.

These equations can be used to calculate the relative distribution between σ_1 and σ_2 if values of N_1, ϵ^1, and δ can be assumed (Adams, 1976). Van Raij and Peech (1972) claimed that the only soil properties needed to calculate the net charge are PZNC and surface area.

Point of Zero Net Charge

Concentration of potential-determining ions and the net surface charge are obviously pH dependent on constant-potential surfaces. There will be a pH at which the densities of positive and negative charges are equal and the surface possesses no net charge (Tinsley, 1974; Keng and Uehara, 1974).

The acidic and basic properties of a solid that influence the location of PZNC are functions of such variables as cation size and valence, the hydration state of the solid, and the geometrical arrangement of the ions. Parks (1965) pointed out that the broad range of isoelectric points in oxides and hydroxides was explained by differences in hydration state, purity, and cation radii.

The PZNC of some pure minerals found in soils can be observed in Table 1 (Adams, 1976). It can be seen that dehydration, dehydroxylation,

and increased crystallinity result in an increase in the PZNC. However, the presence of anionic impurities of pH-dependent, potential-determining ions will decrease the PZNC. Also, structures or compounds which are ion exchangers and have an intrinsic structural charge can be expected to shift the PZNC away from the calculated value by a variable amount. A positive charge density, σ^+, may be expected to move the PZNC in the basic direction, while negative σ^- should move the PZNC in the acid direction (Parks, 1967).

In Fe and Al oxide systems, the Fe and Al ions are not exchangeable, but can be potential-determining ions. In general, the presence of Fe and Al oxides will tend to increase the PZNC of soil toward higher pH values, while the presence of clay minerals with permanent or structural negative charges tends to shift the PZNC of soil to lower pH values (Van Raij and Peech, 1972).

Effects of Specific Adsorption on the PZNC

When specific adsorption of cations or anions occurs at the PZNC, the pH shifts toward higher and lower pH values, respectively (Breeuwsma, 1973). An excess of a specifically adsorbed ionic species will remove pH dependence or change the PZNC to that of the impure species (Parks, 1967). Specific adsorption of ions other than the potential-determining species H^+ and OH^- is related to differences in PZNC between soils and within profiles (Adams, 1976).

Specific adsorption of anions produces a negative surface under otherwise identical conditions. Anions, such as PO_4^{-3}, which are dehydrated and specifically adsorbed by ferric oxides are considered to form a new potential-determining layer by ligand-exchange reactions

Table 1. PZNC of pure minerals found in soils.

Minerals	PZNC	Authors
SiO_2	2.0	Parks and de Bruyn (1962)
Montmorillonite	2.5	Stumm and Morgan (1970)
Kaolinite	4.6	Stumm and Morgan (1970)
Gibbsite	5.0	Stumm and Morgan (1970)
α-$Al(OH)_3$	5.0	Stumm and Morgan (1970)
Magnetite	6.5	Stumm and Morgan (1970)
α-Fe_2O_3	6.7	Stumm and Morgan (1970)
Goethite	7.55	Atkinson et al. (1967)
$Fe(OH)_3$ amorphous	8.5	Breeuwsma (1973)
Hematite	8.45-9.27	Atkinson et al. (1967)
α-Al_2O_3	9.1	Stumm and Morgan (1970)
MgO	12.4	Stumm and Morgan (1970)

with OH- or structural H_2O in the ferric first coordination shell (Atkinson et al., 1967). When P or other anionic chemicals are added to a soil with variable-charge colloids, the adsorbed ("fixed") anions shift the PZNC to lower pH values (Adams, 1976).

Lowering of PZNC in goethite (Hingston et al., 1968) and in tropical soils (Van Raij and Peech, 1972) as a consequence of specific sorption of anions has been clearly demonstrated.

Cation Exchange Capacity

Effect of pH. Change in CEC with change in soil pH has been logically termed pH-dependent CEC. Soil fractions contributing to the degree of pH-dependent CEC were reported to be organic matter and clays which either contain noncrystalline components or have expanding plyllosilicates with hydroxy-Al interlayers (Fiskell and Zelazny, 1971). The cations are held in these systems because of negative charges resulting from ionization of the OH groups attached to Si and Al of broken tetrahedral and octahedral positions and functional groups of organic matter (Wiklander, 1967).

Fiskell and Zelazny (1971) studied the effects of selected soils buffered at several increasing pH values on CEC. The increase in CEC with soil pH was attributed predominantly to the increase in pH-dependent charges on organic matter. Likewise, Fiskell et al. (1964) studied the changes in CEC with change in pH in a Leon fine sand. They found an increase in the CEC of this soil almost linearly with increasing pH. Helling et al. (1964) found that the average increase in CEC of the organic fraction of 60 Wisconsin surface soils was correlated with soil organic matter.

Effect of P adsorption. The CEC of soils is known to increase on treatment with phosphate (Sawhney, 1974). The increase in CEC has been attributed to the replacement of hydroxyl ions by phosphate ions at the surfaces of clay minerals and sesquioxides. Recently, it has been shown that sorption of anions on sesquioxides with surface at constant potential shifts the PZNC to lower pH (Breeuwsma, 1973), thereby, requiring more cations to balance the additional negative charge produced by specific adsorption of anions. Similarly, phosphate sorption caused large increases in the CEC of tropical soils rich in sesquioxides (Mekaru and Uehara, 1972).

Specific sorption of anions on sesquioxides involves not only the replacement of hydroxyl ions but also of water molecules in octahedral coordination on oxide surfaces (Sawhney, 1974). Thus, soil pH is reduced more where a portion of the surface hydroxyls are protonated to form water molecules, and replacement of the water molecules by an anion increases the CEC. Sawhney (1974) found that as the sorbed phosphate increased, the CEC also increased. He attributed the increase in CEC to the replacement of octahedrally coordinated water molecules on sesquioxides surfaces at pH 5, while at higher pH values, increased CEC was caused by replacement of hydroxyl ions.

Crop Response to Lime and P Applications

It has been pointed out (Blue, 1974) that one of the most important considerations in the nutrition of crops in highly weathered Ultisols and Oxisols is the prevalence of P deficiency. Blue (1974) also stated that these soils have relatively high P retention capacities and, therefore, the efficient use of this element is important. The effects of P

and lime on crops have received wide attention. Recently, phosphate adsorption isotherms have been used as a criterion for P applications to tropical soils with high P adsorption capacities.

Fox and Kamprath (1970) found that the effects of large phosphate applications to soils with high phosphate sorption capacities were evident in phosphate sorption isotherms 10 years later. They also used the sorption curves as a basis for fertilizing soils in pot experiments. Reeve and Sumner (1970b) concluded that the wide spectrum of P-fixing abilities of soils indicates that fertilizer recommendations based on direct determination of the amount of P required to raise the status of a soil to a desirable level are likely to be more accurate than those based on an estimate of the amount of available P in the soil per se.

On the other hand, it has been found that lime reduces the adsorption maximum of P in Ultisols by reducing the exchangeable Al (Woodruff and Kamprath, cited by Blue, 1974). However, Amarasiri and Olsen (1973) found that a limed soil had a higher maximum adsorption capacity for P than unlimed soil.

Evans and Kamprath (1970) found that lime increased the growth of corn on mineral soils when Al saturation was greater than 70% and soybean when Al saturation was greater than 30%. Reeve and Sumner (1970a) found that the yield of 'trudan' (Sorghum sudanense) increased with increasing lime and P application rates. They concluded that the increase was due to the reduction of Al toxicity and improvement of P availability.

MATERIALS AND METHODS

Ten soils from Venezuela were used in this study including two Oxisols, a Grossarenic Psammentic Haplustox (Guanipa 5, Anzoategui State), and a Tropeptic Haplustox (Guataparo, Carabobo State); an Ultisol, Typic Paleustult (Guanipa 1, Anzoategui State); three Alfisols, an Ultic Tropudalf (San Cristóbal, Táchira State), an Oxic Haplustalf (Barinas, Barinas State), and an Oxic Tropudalf (Bajo Seco, Miranda State); an Entisol, Ustic Quartzipsamment (El Rocío), an Inceptisol, Fluaquentic Humitropept (Alambre), and a Vertisol, Udorthentic Pellustert (Guanaguanare) from Portuguesa State; and a Aridisol, Haplargid (El Potrero, Lara State). The samples were collected from uncultivated sites (Figs. 1 and 2). The surface 30 cm of soil was mixed (in all samples) except Guanipa 5 for which the A11 (0 to 10 cm) and A21 (10 to 30 cm) horizons were analyzed as separate samples. These soils had a pH range of 3.50 to 5.50, organic matter content of 0.50 to 4.50%, and clay content of 7 to 51%.

To compare soil behavior, Red Bay, a Rhodic Paleudult (horizons A1 and B2t) from Florida, U.S.A., was also used in some analyses. This soil was formed under subtropical conditions and belonged to a highly weathered order.

All samples were air-dried and ground to pass a 2-mm sieve for laboratory and greenhouse experiments.

Fig. 1. Relative location of Venezuela in South America.

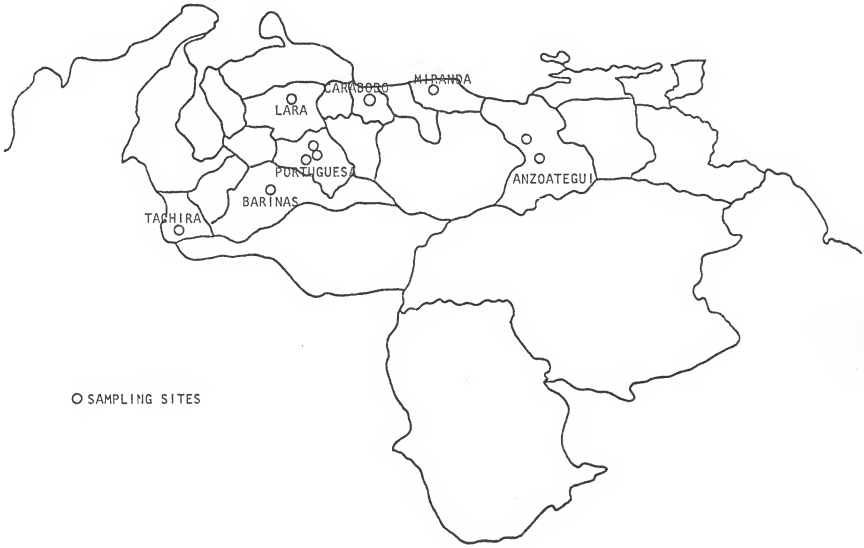

Fig. 2. Relative location of the soil sampling sites in Venezuela.

Soil Physical, Chemical, and Mineralogical Properties

In order to characterize these soils, several physical, chemical, and mineralogical analyses were performed.

Except for Red Bay, particle-size distribution of the soil samples was determined by the pipette method. Moisture equivalent was determined by saturating with water and centrifuging at 1,000 rpm (Beaver et al., 1972). Organic carbon was measured by wet digestion with $K_2Cr_2O_7$-H_2SO_4 (Walkley, 1947).

To prevent interference with X-ray analysis, samples were treated with 30% H_2O_2 to eliminate organic matter. Free Fe oxides were removed by Na-dithionite-citrate-bicarbonate (DCB). After these cementing agents were removed, samples were adjusted to pH 10 with Na_2CO_3 and gently heated to remove any excess of H_2O_2. The sand was separated from silt and clay by wet sieving with a 300-mesh sieve using H_2O adjusted to pH 10 with Na_2CO_3. Clay was separated from silt by repeated decantation after centrifuging at 1,000 rpm for 2 minutes in an International No. 2 centrifuge. The residue was considered to be the silt fraction (Zelazny and Qureshi, 1971).

X-ray Diffraction Analysis

X-ray diffraction analysis criteria were used to identify the crystalline components of the inorganic colloidal separates. This was performed by orienting approximately 200-mg samples of the appropriate clay suspension on several glass slides and leaving them until air dry. One sample was saturated with Mg, one was Mg-saturated glycerol solvated, and the rest were saturated with K, nonheated, and heated to 100 and 500°C for 4 hours. Samples so prepared were analyzed with a Phillips PW1120-96 X-ray diffractometer with Co radiation and scanning from 2 to 50° 2θ.

Fe-oxides Determination

Since Al- and Fe-oxides contribute to P adsorption and to a significant portion of the constant-potential surfaces in many tropical soils, these were determined with Na-DCB. The Fe and Al in the extracts were analyzed by atomic adsorption spectrophotometry in a Perkin-Elmer 303 Spectrophotometer.

Surface Area Determination

Samples for surface-area determination were prepared by saturating the soil with 1N $MgCl_2$. Excess salt was removed with water and the samples were dried at 105°C. The clay was separated by centrifugation and ground to pass a 60-mesh sieve and mixed again with other components (Adams, 1976). Labeled Al dishes were placed in a desiccator over P_2O_5 under vacuum for 6 hours to obtain constant weight. Approximately 1-g samples of soil were then placed in the dishes and brought to constant weight as before. A soil-absorbate slurry was prepared by placing 3 ml of ethylene glycol monomethyl ether (EGME) into the dried sample. The slurry was mixed and placed in a desiccator containing a $CaCl_2$-EGME solvated slurry to equilibrate for 1 hour before applying vacuum (Carter et al., 1965). The desiccator was then evacuated at 0.25 mm Hg for 1 hour. Periodic weights were taken on the soil-adsorbate slurry until constant weight was obtained. The surface area was calculated using the following equation:

$$A = \frac{Wg}{Ws \times 0.00286} \qquad (22)$$

where A = specific surface in m^2/g

Wg = weight of EGME retained by the sample after equilibration in g

Ws = weight of P_2O_5 dried sample in g.

The constant was obtained from the assumption that 2.86×10^{-4} g EGME is required to form a mono-layer on each m^2 of sample (Carter et al., 1965).

Soil Acidity

Soil acidity was determined by potentiometric and conductometric titrations using the following procedure: 5-g soil samples were placed in 200-ml plastic bottles and 50-ml portions of distilled water containing increasing amounts of 0.05N $Ba(OH)_2$, 0.1N NaOH, or 0.1N $Na_2B_4O_7$ were added to the bottles. The pH and electrical conductivity were measured after continuous shaking for 48 hours. Extractable acidity was determined by leaching soil samples with 1N KCl. A 10-g sample was placed in a 125-ml Erlenmeyer flask to which 100 ml of 1N KCl were added. The flask was stoppered and shaken periodically for 2 days. Then, the mixture was filtered through Whatman No. 42 filter paper into a 250-ml volumetric flask and washed with three separate 50-ml portions of 1N KCl. One aliquot of 100 ml was titrated with 0.0458N $Ba(OH)_2$ to pH 8.0. A 50-ml aliquot was analyzed for Al by atomic adsorption. Intensity measurements were also done by reading the pH in H_2O, 1N KCl, 1N K_2SO_4, 0.02M $CaCl_2$-, 4% NaF at 1:2 soil:solvent suspensions. Differences between salt-pH and H_2O-pH were calculated as ΔpH values in which pH (H_2O) was substracted from the pH (salt). All measurements were made using a Beckman pH meter with a combination electrode.

Components of acidity were estimated from the graphs resulting from plotting pH and EC vs meq of base added. Readings were made at inflection points at pH 8 and 10. In conductometric titration curves, inflections were determined at the intersection of two straight lines drawn along the linear portions at the extremities of the curves. End-point

values were multiplied by 0.75 to account for the neutralization factor associated with the formation of aluminate in the $Ba(OH)_2$- treated samples.

Potassium Q/I Characteristics

To determine the Q/I relation of the soil samples, duplicate subsamples of soil were shaken with 50 ml of 0.001M $CaCl_2$ with KCl ranging from 0 to 0.002M in 100-ml centrifuge tubes for 24 hours at room temperature. Equilibrium solution was separated from the soil by centrifugation and analyzed for Na and K with an Ependorf flame spectrophotometer. The gain or loss of K was determined by substracting equilibrium K concentrations from initial K concentrations, assuming that the difference was either adsorbed or released from the soil complexes and converted to meq/100g. The graphs were obtained by plotting the gain or loss of K against the activity ratio of K (AR^k) present in the equilibrium solutions. Cation concentrations were corrected to their chemical activities by using a modified Debye-Huckel equation assuming that all anions were monovalent and Ca, Mg, K, and Na were the only cations present.

$$\log a = \frac{-AZ+Z-\sqrt{I}}{1 + B\alpha \sqrt{I}} \qquad (23)$$

where A = 0.502

Z+ = valence of cation Z- = valence of anion

$\alpha = 2.5 \times 10^{-8}$ cm

$B = 3.9 \times 10^{7}$

a = activity coefficient of electrolytes

I = ionic strength

$I = 1/2 \Sigma Ci Z^2$

Ci = concentration of the ion of charge Zi

Potassium selectivity coefficients were calculated by the Gapon equation as follows:

$$Kg = \frac{K\ (sorbed)}{Ca + Mg\ (sorbed)} \div \frac{\alpha K\ (solution)}{\sqrt{a(Ca + Mg)}\ (solution)} . \qquad (24)$$

Soil equilibrated with 0.001N KCl and 0.001M $CaCl_2$ was extracted three times with NH_4NO_3 and the combined extract was analyzed for K, Ca, and Mg as before. The results were corrected for the entrained solution by analyzing for Cl^- with an anion-specific ion electrode and potentiometer. The determined Cl was partitioned between cations in proportion to their concentrations in the equilibrium solution and these calculated amounts were substracted from measured values in the NH_4NO_3 extracts to obtain the sorbed cations. Cations in solution were determined from the equilibrium solution and their chemical activities were calculated (San Valentín et al., 1972).

Other parameters were derived from the Q/I graphs: PBC^k was calculated from the slope of the linear portion of the curve, the value of AR_o^k from the intercept of the curve when $\Delta K = 0$. Also, ΔK° and K_x were determined as outlined by Beckett and Nafady (1967a) and Lee (1973).

Exchange Properties

Soil CEC was determined by saturating with 1N NH_4OAc (pH 7.0) washing with C_2H_5OH, exchanging the retained NH_4^+ with 1N NaCl, and determining the NH_4^+ by micro-Kjeldahl method (Bremner, 1965). The extract from NH_4OAc saturation was analyzed for Na, K, Ca, and Mg as before. Cation exchange capacity also was determined using the Stern model for double layer and point of zero net charge (PZNC) values.

Point of Zero Net Charge

This analysis is based on the premise that at PZNC, ionic strength will have no effect on potential, i.e., pH. The basic procedure used was that outlined by Adams (1976) except that only two concentrations of NaCl (1.0 and 0.001N) were used. This procedure involves equilibrating several 3-g soil samples for 3 hours in the two concentrations of NaCl to which various aliquots of NaOH or HCl have been added. After equilibration, the samples were centrifuged, the pH of the solution determined, and compared to the pH of the same solution before adding the soil. From this difference in pH, the milliequivalents of H^+ or OH^- adsorbed by the soil were determined and plotted against pH for each salt concentration. The intersection of the graphs was taken as the PZNC of the soil.

Phosphorus Analysis

After centrifugation in a super-speed centrifuge, P in the supernatant solutions was determined. Phosphorus that disappeared from solution was considered to have been sorbed. Phosphorus sorbed was plotted against P in the supernatant solution. After equilibration, soil samples were saved for P release and P fractionation using the Petersen and Corey (1969) modification of the Chang and Jackson (1957) P fractionation procedure. This is a sequential extraction using NH_4Cl, NH_4F adjusted to pH 8.32, NaOH, DCB, and H_2SO_4, to extract water soluble, Al, Fe, reductant soluble, and Ca forms of P. The organic P was estimated from the difference between P extracted with NaOH followed by H_2SO_4 from samples ignited to 600°C for 4 hours compared with nonignited samples. The total P was calculated by adding all the fractions. The P in this and all subsequent P experiments was determined colorimetrically using ammonium molybdate with ascorbic acid as a reducing agent according

to the procedures developed by Watanabe and Olsen (1965). All P determinations were made with a Bauch and Lomb Spectronic 20 spectrophotometer at a wavelength of 880 μm.

Calculations of Thermodynamic Parameters Associated with Adsorption Processes

Thermodynamic parameters ΔG, ΔS, and ΔH were calculated from the variation of the thermodynamic equilibrium constant Ko (or the thermodynamic distribution coefficient) with changes with temperature. This technique was outlined by Biggar and Cheung (1973) and is described in details in Appendix II. Also, ΔG was calculated by using Keq from the relationship of concentration and the inverse of time as outlined by Rydens and Syers (1975). Langmuir and Freundlich equations were used to calculate some values of ΔG related to energy of sorption reactions (Ryden et al., 1977a). All these calculations were performed using a computer, examples of them are shown in Appendix II.

Phosphorus Adsorption Isotherms

Data for plotting P adsorption isotherms were obtained by equilibrating 3-g soil samples for 11 days at 5°C, 25°C, and 40°C in 30 ml of water containing various amounts of KH_2PO_4. Also, isotherms were obtained in samples saturated with KCl and $CaCl_2$ and washed free of Cl^-. These were performed at 25°C using KH_2PO_4 and $Ca(H_2PO_4)_2$, respectively, to keep homoionic systems. Equilibration was carried out in 50-ml plastic centrifuge tubes. Two drops of toluene were added per sample to avoid biological activity. The tubes were shaken in a reciprocal shaker for a 30-minute period daily.

Phosphorus Release

Samples from P adsorption isotherms were extracted 10 times with 0.02 M KCl or 0.02 M $CaCl_2$, shaken for 5 minutes and centrifuged for

25 minutes with a high speed centrifuge. The KCl was used in samples with and without previous K saturation, while $CaCl_2$ was used with the Ca-saturated samples. Phosphorus was analyzed in each extract. The amount was corrected for the initial concentration of the solution left in the soil sample. A sulfur fractionation was performed in the Soil Testing Laboratory of the Soil Department, Facultad de Agronomía, Venezuela, as outlined by Casanova (1974). This is a sequential extraction using HCl and $NaHCO_3$, with and without heat at 500°C.

Lime and Phosphorus Treatments

Lime requirements of the soils were determined by incubating 500-g samples in plastic pots with amounts of $CaCO_3$ equivalent to 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 metric tons/ha. Distilled water was added to the samples to bring the moisture content to moisture equivalent. The pots were closely covered and placed in a greenhouse over a period of 6 months. After incubation, soil samples were dried and pH was determined in H_2O. Lime requirement curves were obtained by plotting pH vs amount of $CaCO_3$ applied.

In order to compare lime requirements, 1N KCl-exchangeable Al^{+3} was determining. The rates of $CaCO_3$ selected for laboratory and greenhouse experiments were 0, 1/2, 1, and 2 times the 1N KCl-exchangeable Al^{+3}.

Phosphorus requirements were calculated from adsorption data obtained from the Langmuir isotherm. The P levels applied to the soil samples were 0, 1/4, 1/2, and 1 times the adsorption maximum calculated from Langmuir isotherms.

Laboratory and Greenhouse Experiments

Samples from nine Venezuelan soils were limed with $CaCO_3$ equivalent to 0, 1/2, 1, and 2 times the 1N KCl-exchangeable Al^{+3}. After 15 days of incubation, four levels of P were established in each soil by adding P as indicated by the appropriate sorption curve, to reach 0, 1/4, 1/2, and 1 adsorption maximum (Table 2). Phosphorus was added as KH_2PO_4 in solution form. The soil was then adjusted with water to moisture equivalent and incubated for 11 days. A portion of sample from each treatment was saved for PZNC and pH determinations.

One-kilogram samples of Guanipa 1, Guanipa 5, and El Potrero soils were place in pots in a greenhouse and planted to sorghum (Sorghum bicolor L.), 'Hybrid Chaguaramas 3' was maintained by frequent irrigation. Plants were harvested 18 days after seeding. All pots received uniform fertilization with N, K, Mg, and micronutrients. The experimental design was two factors (lime and P) at four levels (1, 2, 3, and 4) with three replications and complete randomization. After harvest, soil samples were air-dried, ground to pass a 2-mm sieve, and analyzed for PZNC and pH. Plant material was dried at 60°C and weighed to determine yields.

Statistical Analyses

Analyses of variance were performed for greenhouse experimental data by the General Linear Model procedure (Barr et al., 1976) in the factorial design. Duncan's Multiple Range Test was used to compare individual treatments means. Also, a linear regression study was performed for P adsorption data. Special programs were made to calculate the surface charge with Stern and Gouy-Chapman models, the Q/I parameters for K status in the soils, and thermodynamic parameters.

Table 2. Treatment combinations used in the laboratory and greenhouse experiment with the soils used.

Phosphorus applied		$CaCO_3$ applied‡			
Rate	Designation	1	2	3	4
		Treatment combinations			
0b†	1	11	21	31	41
½b	2	12	22	32	42
¾b	3	13	23	33	43
1b	4	14	24	34	44

†Adsorption maximum (b) from the appropriate Langmuir equation.

‡0, ½, 1, and 2 times the 1N KCl-exchangeable Al.

RESULTS AND DISCUSSION

Soil Characteristics with Emphasis on Surface Charge

The soils selected for this study varied considerably in clay and organic matter contents, CEC, exchangeables bases, and acidity sources. Also, they showed a very large variation in free Fe and Al oxide contents, surface area, clay mineralogy, PZNC, and P and S fractions. The K status was quite different for these soils as shown by the Q/I parameters found with this technique.

Soil organic matter content is a result of biological processes that are controlled by temperature and moisture. The relatively low organic matter contents of these soils was due mainly to the oxidation enhancement of high temperatures. Organic matter colloid translocation was not noted since there was a tendency for lower organic matter contents with depth. The organic matter contents ranged from 0.28 to 4.54% (Table 3). These values are the result of the combined temperature, rainfall, and altitude factors (Westin et al., 1968).

Exchangeable bases in these soils were generally low. Calcium was the predominant ion in all soils (Table 4). Magnesium followed Ca in the exchangeable bases. Potassium values were very low in all soils. Except for San Cristóbal and El Potrero, exchangeable Na was less than 0.1 meq/100g. In general, the highly weathered soils contained less bases than those less weathered. There was a tendency for bases to

Table 3. Physical and chemical properties of soils examined.

Soil	O.M.	Clay	Surface Area	CEC	ECEC	PZNC	Clay Minerals†
	-----%-------		--(m^2/100g)-	-meq/100g--			
Guanipa 1	0.60	6.90	2.7	2.0	1.88	3.25	KA, CH, QZ, Co
Guanipa 5A	0.33	4.40	2.9	1.2	0.64	2.85	KA, QZ, IN, CH, HE
Guanipa 5B	0.28	6.80	2.8	1.1	0.32	3.20	KA, IN, CH, HE, Co
San Cristóbal	1.26	51.00	46.6	23.0	14.10	4.10	VM, KA, QZ, CH, MI
El Rocío	2.72	29.40	39.4	8.3	3.65	3.50	IN, KA, QZ, CH, MI, Co
Bajo Seco	2.52	22.20	27.0	17.0	7.90	3.00	IL, QZ, MI, KA, Co, CH
Guanaguanare	2.49	26.00	54.6	30.4	8.29	3.90	IL, QZ, KA, CH, Co
Guataparo	1.37	30.30	25.0	5.6	3.65	3.75	KA, QZ, IN, GI, Co
Alambre	4.54	24.70	44.0	17.6	7.55	3.50	IN, QZ, KA, GI, Co, CH
El Potrero	3.26	50.60	69.9	11.0	5.40	3.20	KA, QZ, IL, Co
Barinas	1.28	17.70	34.3	6.3	2.40	4.60	KA, QZ, IL, Go
Red Bay A1	2.50	8.20	13.3	7.0	7.98	3.95	IN, GI, KA, QZ, Co
Red Bay B2t	0.60	36.60	25.2	2.2	1.26	4.20	KA, IN, GI, QZ

†The following abbreviations are used: KA=kaolinite; CH=chlorite; QZ=quartz; VM=vermiculite; IN= intergrade; HE=haematite; Go=goethite; MI=mica; GI=gibbsite; Co=corundum; IL=illite.

Table 4. Exchange properties and free oxides of the soils examined.

Soil	Fe oxides	Al oxides	Exchangeable Al 1N KCl	Exchangeable Acidity $Ba(OH)_2$	Exchangeable Bases Na	K	Ca	Mg
	----------%----------		----------meq/100g----------					
Guanipa 1	0.93	0.93	0.021	1.40	0.02	0.08	0.36	0.35
Guanipa 5A	0.75	1.03	0.035	1.30	0.01	0.04	0.35	0.25
Guanipa 5B	0.87	0.76	0.040	1.70	0.01	0.02	0.20	0.10
San Cristóbal	3.57	3.45	0.141	10.00	0.82	0.50	7.50	6.10
El Rocío	3.10	2.30	0.600	3.30	0.06	0.15	3.30	0.20
Bajo Seco	3.07	1.90	0.050	9.00	0.01	0.55	6.30	1.03
Guataparo	3.07	1.52	1.300	4.36	0.07	0.25	1.05	0.37
Guanaguanare	3.39	2.60	0.080	6.00	0.06	0.19	5.10	3.00
Alambre	3.46	1.73	3.900	12.00	0.02	0.15	2.40	1.00
El Potrero	4.29	2.90	3.020	13.00	0.80	0.30	1.10	1.00
Barinas	1.82	1.50	0.100	4.95	0.07	0.15	0.82	0.69
Red Bay A1	1.29	0.64	0.550	16.01	0.02	0.26	5.72	1.00
Red Bay B2t	1.79	0.89	0.430	3.40	0.01	0.05	0.50	0.33

decrease with depth. These values were expected because of the low pH of all soils. Cation exchange capacity values were variable (Table 3) and higher than effective CEC (ECEC). Guanipa 1 showed CEC equal to ECEC. Cation exchange values ranged from 1.1 to 30.4 meq/100g. The values of CEC were due to the contribution of organic matter and clay content in these soils. The magnitude of permanent negative charge would be expected to vary according to the degree of tetrahedral substitution in the clay mineral. The amounts of Al and Fe oxides present in addition to the presence of crystalline colloidal species with low pH-dependent charges would considerably influence CEC measurement at pH 7.00.

Free Fe-oxide values ranged from 0.75 to 4.29%. Aluminum oxides ranged from 0.64 to 3.45% (Table 4). These values reflected the stage of soil weathering. These results indicate a loss of Si due to the acidic environment and an enrichment in the Al and Fe oxides. A tendency of these values to decrease with depth indicated that Fe and Al have been released from primary minerals and translocated by percolating water to lower horizons.

Surface-area values ranged from 2.7 to 69.9 $m^2/100g$ (Table 3) and were related to organic matter and clay content in these soils. The highest value was obtained for the Aridisol and the lowest for the sandy Ultisol. These soils had increasing surface area with depth. The migration of fine particles in soil formation processes can account for these results (Luque, 1975).

The amount of clay in soils depends upon the soil-forming factors including parent material, relief, time, biotic, and climate. The clay

contents in the soils studied ranged from 4.40 to 51.00% (Table 3). Clay content tended to increase with depth, indicating downward movement and accumulation in lower horizons.

Clay Mineralogy

Abundance of kaolinite and quartz is indicative of parent materials in their last weathering stage. Oxisols which represent the extreme of pedogenic weathering have traces of aluminosilicates such as intergrade (Table 3). These soils contain various Fe and Al oxides (gibbsite, hematite, and goethite) as evidenced by 4.83, 3.67, and 4.96 Å peaks, respectively, and in some cases, chlorite. Soils Guanipa 5 and Guataparo represent this order. Weathering has been so severe that only resistant minerals (quartz 4.2 and 3.35 Å, and corundum 3.47, 2.55, and 2.08 Å), and highly resistant layer silicates remain.

Clay fractions with Ultisols were dominated by kaolinite and intergraded phyllosilicates (Guanipa 1 and Red Bay). Kaolinite was identified by first order spacing 7.0 Å. A band in 11.6 to 12.6 Å region was assumed to represent intergrade minerals because of their persistence after heating. Guanipa 1 showed some chlorite. The peaks at 13.6 to 14.3 Å without expanding at Mg treatment were assumed to be chlorites.

Alfisols (San Cristóbal, Barinas, and Bajo Seco) tended to have a somewhat wide-ranging clay mineral suite. Barinas (Haplustalf) showed predominance of kaolinite, followed by quartz and illite, and some amount of goethite, while Bajo Seco (Tropudalf) had illite, quartz, mica, and some amounts of kaolinite, corundum, and chlorite. Finally, San Cristóbal (Tropudalf) showed vermiculite, in addition to kaolinite, quartz, mica, and chlorite. Vermiculite was concluded to be present by the Mg-saturation 14 to 15 Å spacing and a 10.0 Å spacing after heating to 500°C.

The presence of these minerals may have been the result of a more base-enriched environment, and to low rainfall and a distinct dry season (Westin et al., 1968; Zelazny and Calhoun, 1971). Entisols and Inceptisols exhibited inherited minerals such as mica, intergrade layer silicates and chloride in addition to kaolinite and quartz (Table 3).

Point of Zero Net Charge

The PZNC values for the soils examined ranged from pH 2.85 to 4.60 (Table 3). The Guanipa 1 and Barinas soils were the lowest and highest, respectively. These values tended to increase with soil depth and weathering. If a PZNC range of pH 3.5 to 5.0 is characteristic of soils dominated by constant surface-potential colloids as proposed by Keng and Uehara (1974), those soils, except for Guanipa 1, should belong to this group. The lower PZNC values for these soils were due to the presence of organic matter in their surface horizons. It has been shown by Adams (1976) that the narrowed range of PZNC in tropical and temperate regions was due to the interlayered Al and organic matter.

Phosphorus and Sulfur Fractionation

Phosphorus fractions as determined by the Peterson and Cory (1969) method showed dominant P forms to be Fe-P, Al-P, and Ca-P. All the soils, except Guanipa 1 and 5A had lower amounts of Al-P than Fe-P. This may have been due to the lower solubility product of Fe-P. Also, aging may have been responsible because of the high Fe oxide content (Yuan et al., 1960). Soluble P was not detected in these soils. Most of the P was in the organic form (Table 5).

On the other hand, S fractionation (Casanova, 1974) showed that S was mainly in the clay and organic forms (Table 6). These values of S in the clay fraction suggested that these soils have a high capacity to adsorb and exchange phosphate (Casanova, 1974).

Table 5. Phosphorus fractionation of the virgin soils examined.

Soil	Organic P	Soluble P	Al-P	Fe-P	Prs	Ca-P	P Total
	ppm						
Guanipa 1	43.2	T[†]	14.6	14.1	T	5.6	75.1
Guanipa 5A	28.1	T	12.2	9.0	T	5.6	56.2
Guanipa 5B	28.1	T	8.5	9.0	T	3.5	47.8
San Cristóbal	197.3	T	31.5	36.0	T	84.7	331.3
El Rocío	422.7	T	98.2	123.8	16.2	70.0	776.8
Bajo Seco	147.9	T	15.2	22.5	T	9.1	178.7
Guataparo	281.8	T	26.8	56.3	T	11.9	369.8
Guanaguanare	380.4	T	47.0	58.5	18.3	44.8	524.9
Alambre	285.0	T	15.9	31.2	4.6	19.6	382.2
El Potrero	335.0	T	21.4	36.0	T	14.0	410.1
Barinas	172.0	T	15.9	19.1	T	11.5	211.0
Red Bay A1	118.7	T	17.1	29.3	T	7.0	176.9
Red Bay B2t	290.1	T	18.0	27.0	T	9.8	343.9

[†]The letter T indicates trace quantities.

Table 6. Sulfur fractionation of some of the virgin soils examined.

Soil	Organic S	Available S	Clay - S	Total S
	ppm			
Guanipa 1	T	86.0	62.0	119.0
San Cristóbal	33.3	54.7	42.21	87.3
El Rocío	13.0	53.3	47.43	66.6
Bajo Seco	1042.0	19.0	57.0	1231.0
Guataparo	76.0	91.0	63.0	170.0
Guanaguanare	40.0	40.0	30.0	80.0
Alambre	40.0	26.6	15.0	66.6
El Potrero	42.0	53.3	48.0	95.3
Barinas	71.0	90.0	51.0	161.0

The experiment carried out to determine the temperature of incubation effect on P fractions after an 11-day equilibrium period showed that most of the P was in the NH_4F and NaOH extracts and was assumed to be in the Al and Fe forms, respectively (Tables 7 through 19). Only small amounts of P were found in the NH_4Cl and H_2SO_4 extracts which represent water-soluble and Ca phosphate forms (Fig. 3). The phosphate applied, even at high rates, was fixed by Al and Fe. This was due to the fact that in acid soils the applied P precipitates or is adsorbed as Fe-P and Al-P (Yuan et al. 1960).

In the Guanipa 5B (A12 horizon), at highest P applied and 40°C, the amount of P in the NaOH extract was more than in the NH_4F extract (Table 9). This indicated that P in this soil tended to form Fe-P rather than Al-P because of the lower solubility product of Fe phosphate or by a shifting of P from the Al-P form to Fe-P form induced by the higher temperature (Yuan et al., 1960).

The ratios of Al-P to Fe-P broadened with increasing P applied. It has been pointed out that kaolinite can function in the fixation of P by bonding of P to Al at the broken edges. This could have been the case in soils with kaolinite as the dominant clay mineral (Yuan et al., 1960).

The pH and pH_2PO_4 of the different ionic systems at 25°C are shown in Tables 20 through 28. The pH_2PO_4 values were very low at high equilibrium P concentrations. This indicated that precipitation of Al and Fe phosphates such as strengite and variscite can occur. An experiment was carried out to observe the effect of high temperature on Al- and Fe-phosphate precipitation in the nonsaturated system with the highest

Table 7. Effect of incubation temperature on phosphorus fractions in a typic Paleustult from Anzoategui State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	11.04	9.41	8.35	1.67
100	56.76	19.98	8.35	1.39
500	104.4	30.14	8.6	3.29
1000	145.7	25.59	7.97	2.46
		25°C		
0	10.88	9.66	15.25	1.84
100	80.62	30.32	6.96	6.39
500	125.75	37.93	11.19	5.68
1000	151.8	37.93	8.6	4.90
		40°C		
0	6.1	9.7	9.88	1.92
100	71.77	22.8	13.81	2.73
500	157.9	26.78	16.65	2.73
1000	276.5	28.82	17.88	2.87

Table 8. Effect of incubation temperature on phosphorus fractions in a Grossarenic Psammentic Haplustox from Anzoategui State, Venezuela (A11 horizon) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	11.7	14.21	8.64	----
100	160.4	10.62	8.60	----
500	326.11	11.21	8.60	----
1000	380.0	13.97	9.88	----
		25°C		
0	12.2	9.0	9.80	1.80
100	64.25	20.12	4.83	3.28
500	115.5	23.58	7.34	4.85
1000	140.0	27.10	3.60	4.58
		40°C		
0	5.51	14.67	12.50	0.37
100	66.97	26.01	16.38	0.78
500	143.61	30.79	17.75	1.26
1000	388.17	34.85	19.27	1.26

Table 9. Effect of incubation temperature on phosphorus fractions in a Grossarenic Psammentic Haplustox from Anzoategui State, Venezuela (A12 horizon) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	8.85	6.88	8.60	----
100	64.25	13.17	8.60	0.50
500	144.9	15.01	8.35	0.62
1000	179.0	20.11	8.60	0.88
		25°C		
0	8.5	9.0	4.8	2.2
100	77.17	25.74	4.83	2.31
500	128.7	31.40	4.83	2.51
1000	138.8	23.58	4.83	1.12
		40°C		
0	4.37	18.25	13.16	1.01
100	94.02	301.41	19.00	1.52
500	138.62	315.86	19.27	1.79
1000	186.84	367.0	10.00	1.79

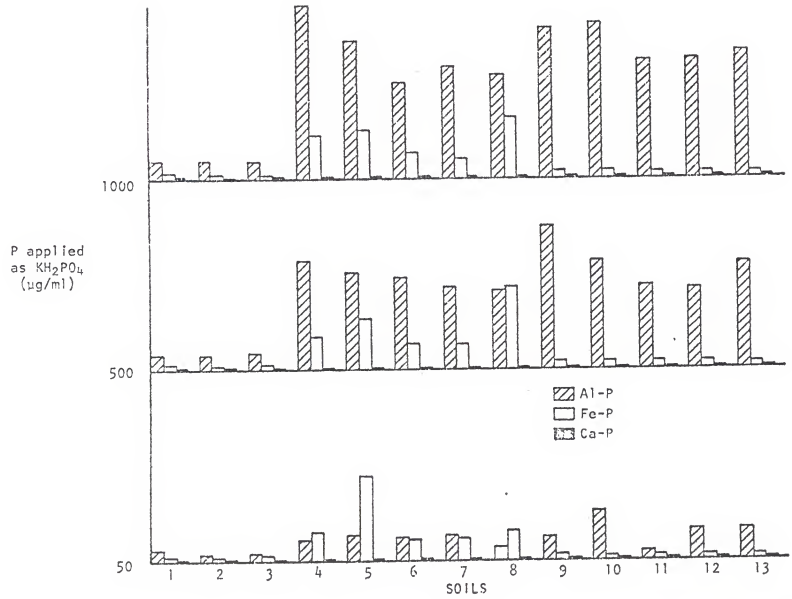

Fig. 3. Phosphorus fractions as affected by P concentrations after an 11-day equilibrium period of 25°C. (1=Guanipa 1; 2=Guanipa 5A; 3=Guanipa 5B; 4=San Cristóbal; 5=El Rocío; 6=Bajo Seco; 7=Guataparo; 8=Guanaguanare; 9=Alambre; 10=El Potrero; 11=Barinas; 12=Red Bay A1; and 13=Red Bay B2t.)

Table 10. Effect of incubation temperature on phosphorus fractions in an Ultic Tropudalf from Táchira State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	10.4	40.9	14.5	1.84
100	283.7	188.6	25.3	3.40
500	856.1	293.1	31.0	4.00
1000	1179.0	357.1	34.2	9.50
		25°C		
0	26.5	44.70	1.2	----
100	311.7	255.0	9.25	----
500	908.8	264.3	15.15	----
1000	1454.3	372.3	15.15	----
		40°C		
0	8.94	42.6	1.3	1.76
100	680.4	264.8	44.0	2.6
500	1124.3	294.7	72.8	3.1
1000	2196.3	301.4	84.1	3.7

Table 11. Effect of incubation temperature on phosphorus fractions in a Ustic Quartzipsamment from Portuguesa State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	28.9	91.0	52.55	2.73
100	342.8	235.79	87.0	12.58
500	788.2	377.1	96.8	10.61
1000	1016.8	782.6	102.3	7.75
		25°C		
0	35.8	41.7	51.9	5.40
100	394.6	612.8	60.6	5.65
500	808.1	420.7	64.6	5.68
1000	1170.7	480.8	64.6	5.68
		40°C		
0	34.5	47.26	89.5	2.9
100	658.4	217.7	132.1	3.15
500	1361.4	329.1	174.2	4.6
1000	1650.6	387.5	175.3	4.5

Table 12. Effect of incubation temperature on phosphorus fractions in an Oxic Tropudalf from Miranda State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	15.9	47.1	2.40	2.56
100	582.3	126.4	45.37	5.19
500	756.9	188.6	45.73	6.59
1000	886.0	270.9	52.91	4.59
		25°C		
0	18.2	201.4	8.6	2.7
100	309.0	396.9	64.6	7.4
500	775.5	241.4	79.8	12.2
1000	810.3	204.0	56.6	11.5
		40°C		
0	12.5	39.9	2.8	6.1
100	420.6	338.2	75.0	5.5
500	870.8	347.5	97.8	5.4
1000	938.5	420.6	113.1	5.8

Table 13. Effect of incubation temperature on phosphorus fractions in a Tropeptic Haplustox from Carabobo State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	9.3	1.5	11.2	2.4
100	214.5	47.2	17.6	3.9
500	667.6	83.3	24.9	3.4
1000	956.1	82.3	24.9	2.8
		25°C		
0	5.2	153.0	1.2	2.4
100	325.3	181.9	17.2	4.0
500	676.6	194.6	6.1	3.5
1000	930.0	158.1	8.6	3.2
		40°C		
0	10.6	24.0	19.4	2.6
100	432.0	96.5	32.2	3.6
500	694.5	148.9	37.3	5.5
1000	1175.9	176.4	37.3	16.6

Table 14. Effect of incubation temperature on phosphorus fractions in an Udorthentic Pellustert from Portuguesa State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	19.5	17.7	44.3	6.7
100	382.5	97.4	44.3	5.9
500	933.4	132.3	51.0	10.8
1000	1007.0	163.6	71.2	9.5
		25°C		
0	24.7	68.0	23.1	2.1
100	233.0	441.1	129.6	3.7
500	662.0	676.6	129.6	4.0
1000	868.7	511.7	150.9	4.8
		40°C		
0	17.3	53.9	74.8	4.5
100	534.3	490.3	162.0	5.2
500	1253.8	609.2	206.6	5.9
1000	1896.2	688.2	226.5	8.1

Table 15. Effect of incubation temperature on phosphorus fractions in a Fluaquentic Humitropept from Portuguesa State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	6.6	31.4	33.4	3.7
100	406.8	62.3	49.3	6.8
500	1158.5	61.3	55.1	7.5
1000	712.1	66.5	54.8	11.4
		25°C		
0	15.9	9.8	67.7	2.0
100	456.9	82.4	52.9	4.3
500	1186.2	87.0	59.5	4.1
1000	1247.1	357.2	70.8	4.8
		40°C		
0	26.9	36.2	37.3	1.5
100	971.2	351.4	58.6	1.5
500	2502.9	382.3	80.3	3.5
1000	3014.5	484.6	83.3	3.4

Table 16. Effect of incubation temperature on phosphorus fractions in a Haplargid from Lara State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	9.3	23.4	33.8	3.6
100	345.3	55.9	37.3	87.0
500	997.4	62.3	40.9	87.0
1000	1284.3	59.4	42.3	87.0
		25°C		
0	10.3	57.2	24.9	9.3
100	513.8	185.4	32.1	4.9
500	908.8	277.2	38.1	6.1
1000	1300.1	311.5	51.1	9.0
		40°C		
0	16.4	59.4	37.3	8.7
100	673.0	320.3	41.9	8.7
500	1576.5	333.6	45.7	8.7
1000	2111.6	382.3	56.5	10.5

Table 17. Effect of incubation temperature on phosphorus fractions in an Oxic Haplustalf from Barinas State, Venezuela (0-30 cm) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	6.9	16.2	22.1	3.9
100	262.4	28.0	29.4	6.1
500	696.6	52.2	29.6	6.5
1000	840.9	41.1	30.2	7.3
		25°C		
0	24.6	15.3	29.4	3.1
100	252.6	69.7	35.4	2.7
500	702.9	105.2	35.4	2.5
1000	988.4	123.8	40.9	3.0
		40°C		
0	13.1	24.4	27.2	6.4
100	361.3	118.7	33.8	9.3
500	788.2	171.2	46.6	10.6
1000	1231.1	210.8	48.3	10.6

Table 18. Effect of incubation temperature on phosphorus fractions in a Rhodic Paleudult from Florida, U.S.A. (A1 horizon) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	9.7	21.3	17.8	1.6
100	294.3	38.4	23.6	3.0
500	763.4	37.4	30.9	3.7
1000	992.5	72.6	25.7	4.3
		25°C		
0	37.3	27.7	17.8	7.4
100	473.0	110.1	30.2	8.7
500	916.7	152.2	35.7	8.5
1000	1003.2	181.3	34.9	9.7
		40°C		
0	28.6	36.7	16.5	3.9
100	691.5	220.0	35.7	6.4
500	2313.6	270.9	46.6	10.0
1000	2227.3	286.6	54.7	9.8

Table 19. Effect of incubation temperature on phosphorus fractions in a Rhodic Paleudult from Florida, U.S.A. (B2t horizon) after applying several solution concentrations of phosphorus.

P applied as KH_2PO_4	Al-P	Fe-P	Prs	Ca-P
		ppm		
		5°C		
0	11.3	20.5	32.5	4.0
100	385.0	28.0	33.8	7.6
500	765.8	34.0	35.7	7.7
1000	1145.3	31.7	36.0	7.7
		25°C		
0	21.0	22.6	21.3	5.3
100	410.5	63.5	30.2	5.4
500	871.2	92.6	41.3	4.7
1000	1052.3	110.1	34.1	3.9
		40°C		
0	12.6	31.3	27.9	6.0
100	445.0	220.6	43.9	11.7
500	1121.4	228.8	47.5	11.7
1000	1443.8	244.9	61.5	15.6

Table 20. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for a typic Paleustult from Anzoategui State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	3.61	6.75	4.41	5.95	3.52	5.40
50	2.84	6.35	3.14	5.85	3.22	5.30
100	2.52	5.85	2.86	5.65	2.92	5.00
200	2.22	5.70	2.61	5.50	2.62	4.55
700	1.68	5.30	1.93	5.10	1.92	3.70
1000	1.55	5.20	1.52	4.80	1.58	3.40

Table 21. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for an Ultic Tropudalf from Táchira State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.11	6.60	3.67	6.50	3.71	6.15
50	6.05	3.64	6.00	3.64	5.60	
100	2.80	5.70	3.08	6.10	3.30	5.30
200	2.40	5.55	2.79	5.90	2.88	5.00
700	1.75	5.20	2.03	5.60	2.02	4.90
1000	1.58	5.10	1.69	5.25	1.67	4.60

Table 22. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for an Ustic Quartzipsamment from Portuguesa State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.58	6.75	3.94	6.70	3.62	6.10
50	3.55	6.70	3.43	6.30	3.55	6.15
100	3.05	6.50	3.08	6.05	3.40	6.10
200	2.48	5.70	2.82	6.25	3.31	5.45
700	1.75	5.15	2.00	6.90	2.04	4.70
1000	1.58	5.10	1.55	5.35	1.67	4.30

Table 23. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for an Oxic Tropudalf from Miranda State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.26	7.35	3.51	6.85	4.07	6.50
50	3.56	7.25	3.12	6.80	3.53	6.30
100	2,97	7.05	2.94	6.70	3.16	5.80
200	2.46	6.60	2.69	6.40	2.77	5.40
700	1.74	5.60	1.97	5.80	1.98	4.80
1000	1.55	5.45	1.60	5.50	1.68	4.30

Table 24. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for an Udorthentic Pellustert from Portuguesa State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.53	7.45	3.93	7.60	3.71	6.90
50	3.95	7.75	3.34	7.20	3.63	6.70
100	3.03	7.70	3.00	7.10	3.23	6.35
200	2.69	6.90	2.72	6.35	2.83	5.80
700	1.82	6.05	2.02	6.00	1.98	4.50
1000	1.61	5.60	1.62	5.60	1.67	4.20

Table 25. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for a Tropeptic Haplustox from Carabobo State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.28	6.05	3.86	5.55	3.71	6.00
50	3.12	5.45	3.30	5.55	3.58	5.70
100	2.72	5.40	3.01	5.62	3.21	5.55
200	2.33	5.35	2.81	5.55	2.80	5.25
700	1.71	5.10	1.98	5.20	1.95	4.60
1000	1.54	5.05	1.57	5.05	1.68	3.90

Table 26. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for a Fluaquentic Humitropept from Portuguesa State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	5.01	6.55	3.78	6.00	3.72	5.60
50	3.85	6.75	3.51	6.00	3.68	5.30
100	3.03	5.55	3.18	5.35	3.50	4.80
200	2.51	4.76	2.88	5.25	3.03	4.50
700	1.78	4.60	2.04	5.30	2.07	4.00
1000	1.59	4.65	1.60	4.90	1.67	3.80

Table 27. Values of pH_2PO_4 and pH at equilibrium with different ionic system after P adsorption for a Haplargid from Lara State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.53	4.80	3.58	5.65	3.75	4.80
50	3.38	4.70	3.37	5.45	3.71	4.70
100	2.88	4.30	3.06	5.40	3.35	4.40
200	2.43	4.55	2.81	5.20	2.91	4.30
700	1.75	4.50	1.99	4.80	2.07	3.80
1000	1.58	4.50	1.60	4.65	1.66	3.70

Table 28. Values of pH_2PO_4 and pH at equilibrium with different ionic systems after P adsorption for an Oxic Haplustalf from Barinas State, Venezuela.

P added	Nonsaturated		K saturated		Ca saturated	
	pH_2PO_4	pH	pH_2PO_4	pH	pH_2PO_4	pH
-µg/ml-						
10	4.41	6.75	3.64	6.55	3.75	6.95
50	3.13	6.30	3.40	6.50	3.74	6.85
100	2.70	6.00	3.02	6.30	3.36	6.50
200	2.34	5.85	2.64	6.00	3.27	5.95
700	1.71	5.50	1.95	5.60	2.00	5.00
1000	1.54	5.40	1.57	5.35	1.67	4.65

P concentration. Soil samples were autoclaved first for 20 hours at 120°C and then for 40 hours at 120°C. X-ray diffraction patterns showed the presence of strengite 20-hour treatment in some soils but no variscite. For the 40-hour treatment, both variscite and strengite were present, except in the San Cristóbal and El Rocío soils. These minerals were identified by the strong peaks at 16.4, 20.6, and 26 Å (Blanchard, 1974). As has been pointed out by Webber (1978), hydrous aluminum oxide plays an important role in binding phosphate in acid soils and clays; variscite formation is expected in acid tropical soils, but amorphous Al phosphate would be expected to persist indefinitely in other acid soils (Webber, 1978).

In these tropical acid soils, high P application may tend to produce precipitation of $(AlFe)PO_4$ compounds. This could explain why P is more deficient in tropical acid soils than in acid soils from temperate regions.

Negative Surface Charge

Acidity

To determine the release of protons in these surfaces a complete study of acidity sources was carried out through intensity and extractable acidity measurements.

The pH of a soil suspension is sometimes lowered or increased by the addition of an electrolyte. Electrolytes such as KCl, K_2SO_4, and $CaCl_2$ lower the pH while higher pH values are found with NaF in soil suspension. The sign of the difference between soil pH in KCl, an indifferent electrolyte, and soil pH in water has been related to the sign of the net surface change of soil colloids (Mekaru and Uehara,

1972). The difference between pH in KCl and K_2SO_4 has been associated with anion adsorption (Adams, 1976). The pH in NaF has been related to the release of hydroxyl groups in Andosols (Calhoun and Carlisle, 1971).

The measurements of pH showed a wide range of variation from very strongly acid in El Potrero to weakly acid in Guanipa 5A. All pH values in water in the soils examined were decreased with addition of KCl. Except for Guataparo and El Potrero soils, pH values in water were decreased with addition of K_2SO_4 and $CaCl_2$. The pH values in NaF ranged from 8.40 to 10.25. These values tended to be higher in the Oxisols, Ultisols, and Alfisols than in the less weathered soils (Table 29).

The negative values of $\Delta pH(KCl-H_2O)$ indicated that these soils had a net negative charge. The negative value of $\Delta pH(KCl-K_2SO_4)$ indicated a high capacity of those soils to exchange anions and, therefore, to fix phosphate. The $\Delta pH(KCl-K_2SO_4)$ values were caused by the fact that the amount of hydroxyl ions displaced by sulphate anions was greater than the Al displaced by K ions (Adams, 1976). The very high negative values of $\Delta pH(H_2O-NaF)$ indicated a large displacement of hydroxyl groups linked to Al and Fe oxides in these soils (Calhoun and Carlisle, 1971).

The values of extractable acidity and Al with 1N KCl and those from potentiometric and conductometric titrations are shown in Table 30. The 1N KCl-exchangeable Al and acidity titrated with $Ba(OH)_2$ ranged from 0.02 to 3.90 and 1.30 to 16.01 meq/100g, respectively. The higher values of exchangeable acidity compared to exchangeable Al^{+3} may have been caused by the contribution of polymeric Al and aluminate reactions that occurred during shaking and titration in the $Ba(OH)_2$ (Dewan and Rich, 1970).

For Venezuelan soils potentiometric and conductometric titration values with NaOH, $Ba(OH)_2$, and $Na_2B_4O_7$ are shown in Table 30. At pH 8.00,

Table 29. Soil reaction with selected electrolyte and calculated ΔpH values for the soils examined.

Soil	pH					ΔpH		
	H_2O	KCl	K_2SO_4	NaF	$CaCl_2$	KCl-H_2O	KCl-K_2SO_4	H_2O-NaF
Guanipa 1	5.45	4.36	4.84	8.60	4.64	-1.09	-0.48	-3.15
Guanipa 5A	5.68	4.47	5.01	8.45	4.80	-1.19	-0.54	-2.77
Guanipa 5B	5.58	4.34	5.02	9.10	4.60	-1.24	-0.68	-3.52
San Cristóbal	5.50	3.98	4.53	9.20	4.69	-1.52	-0.55	-3.70
El Rocío	4.50	3.94	4.48	8.95	4.51	-0.56	-0.54	-4.45
Bajo Seco	5.25	4.75	5.07	8.75	5.12	-5.12	-0.32	-3.50
Guanaguanare	5.00	4.55	5.00	8.60	5.03	-0.45	-0.45	-3.60
Guataparo	4.03	3.90	4.43	9.55	4.32	-0.40	-0.53	-5.25
Alambre	4.20	3.57	4.08	9.15	4.13	-0.63	-0.51	-4.95
El Potrero	3.55	3.44	3.95	8.80	3.82	-0.11	-0.51	-5.25
Barinas	5.10	4.37	5.01	9.85	5.03	-0.73	-0.64	-4.75
Red Bay A1	5.30	4.61	5.20	9.75	5.20	-0.69	-0.59	-4.45
Red Bay B2t	5.50	5.00	5.50	10.25	5.40	-0.50	-0.50	-4.75

Table 30. Acidity from potentiometric titrations at pH 8.00 and conductometric titrations with NaOH, $Ba(OH)_2$, and $Na_2B_4O_7$ for the Venezuelan soils examined.

Soil	Potentiometric titration at pH 8.00 with			Conductometric titration with		
	NaOH	$Ba(OH)_2$	$Na_2B_4O_7$	NaOH	$Ba(OH)_2$	$Na_2B_4O_7$
	meq/100g					
Guanipa 1	2.0	2.6	1.6	22.8	23.8	12.0
Guanipa 5A	2.0	2.8	1.6	27.6	27.6	20.0
Guanipa 5B	1.2	1.6	1.6	30.4	26.1	12.0
San Cristóbal	12.8	6.0	8.0	50.4	39.6	12.0
El Rocío	8.4	10.6	10.6	46.4	34.8	10.4
Bajo Seco	7.2	6.0	6.0	45.6	24.4	7.0
Guanaguanare	11.2	10.0	10.0	38.4	32.7	44.8
Guataparo	7.6	6.4	7.6	28.4	19.8	24.4
Alambre	11.2	13.0	13.0	61.6	31.5	58.0
El Potrero	16.4	14.0	16.0	46.0	41.7	22.8
Barinas	3.6	4.4	4.0	24.0	28.5	24.4

the acidity titrated ranged from 1.2 to 16.4 meq/100g in NaOH, from 1.6 to 14.0 in $Ba(OH)_2$, and from 1.6 to 16.0 in $Na_2B_4O_7$. The soils with lowest and highest values were Guanipa 5B and El Potrero. The acidity titrated at this point was probably due to dissociation of organic matter groups, SiOH groups, and exchangeable and polymeric Al (Jackson, 1963). The values obtained with $Ba(OH)_2$ and NaOH were similar except for the San Cristóbal soil. This suggested that there was no exchangeable or bonding of H to permanent negative charge in these soils (Shainberg and Dawson, 1967).

As pointed by Shainberg and Dawson (1967), the acidity titrated with $Na_2B_4O_7$ is closely related to permanent negative charge (Table 3). The values obtained with conductometric titrations indicated high values of exchangeable Al, probably caused by dissolution of minerals with release of structural Al or reaction of bases with organic acids (Dewan and Rich, 1970). The higher values of extractable acidity shown by the soils compared to 1N KCl exchangeable Al is good evidence of Al retention by organic matter. There was no evidence of exchangeable H in potentiometric and conductometric titration curves. The low values of Al in some soils were probably due to the fact that Al was not exchangeable by 1N KCl, even though potentiometric and conductometric titrations detected it in those soils.

Lime Requirement

El Potrero and Alambre soils had the highest buffer capacities and lime requirements (Fig. 4). These soils reached pH5.80 only after application of 10 metric tons of $CaCO_3$/ha. Guanipa soil had the lowest buffer capacity because with 1 metric ton/ha it reached pH 6.60 and with 2 metric tons/ha, pH 7.30. In general, lime requirements were as expected because

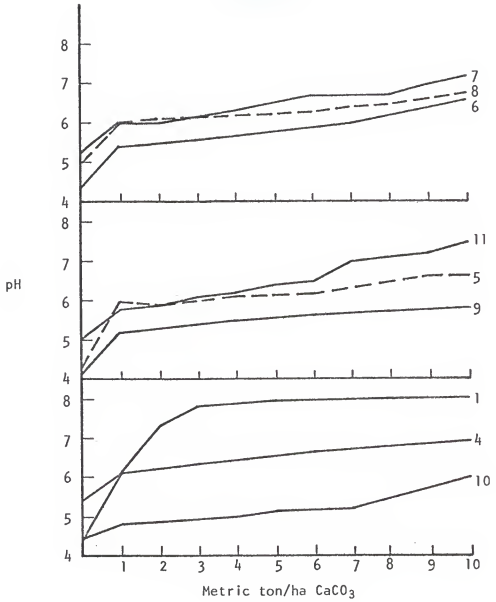

Fig. 4. Effects of $CaCO_3$ applications after 6 months incubation period. (Guanipa 1=1; San Cristóbal=4; El Rocío=5; Bajo Seco=6; Guataparo=7; Guanaguanare=8; Alambre=9; El Potrero=10; and Barinas=11.

soils differed in amounts of organic matter and clay. From the results, one can calculate the amount of lime needed to adjust these soils to the desired pH. The amounts of $CaCO_3$ needed to neutralize exchangeable Al (pH 5.50) varied with soils and in El Potrero soil was approximately 10 metric tons/ha (Fig. 4).

Potassium Q/I Parameters

To investigate ionic selectivity of the negative surface charge in these soils, a study of adsorption-desorption of K related to Ca was conducted. The Beckett Q/I relationship was studied. The parameters found were not related to the position of soil in soil classification systems, but to the minerals predominating in the clay fractions.

The shapes of the curves resulting from Q/I relationships were the same for all soils studied (Fig. 5). Exchangeable K ranged from 0.02 to 0.05 meq/100g (Table 31). The highest exchangeable K values occurred in the less weathered soils. The presence of mica (Table 3) could explain the highest values of exchangeable K. The AR_e^k values ranged from 0.0017 in Guanipa to 0.028 in Red Bay A1. It is assumed that those soils with low AR_e^k values may have high K-fixation capacities. Red Bay B2t showed a value of 0.01 meq/100g for $\Delta K°$ while Bajo Seco had 0.3 meq/100g. The high value of $\Delta K°$ for the Bajo Seco soil was probably a consequence of the presence of illite and other K fixing minerals. The highest values of PBC^k were found in San Cristóbal and Guanaguanare soils. San Cristóbal had a higher PBC^k than Guanaguanare perhaps because of the higher clay content. These two soils had the highest CEC values, the difference in PBC^k values between them was probably caused by vermiculite in the San Cristóbal soil and illite in Guanaguanare.

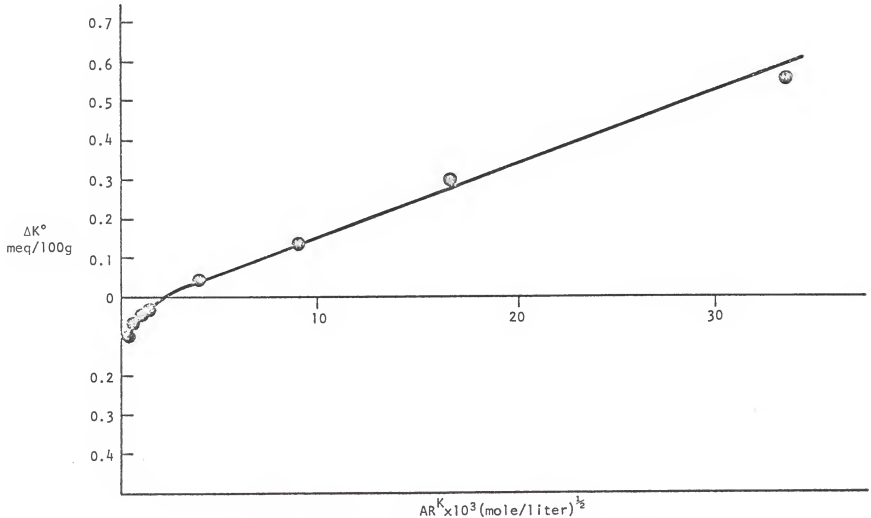

Fig. 5. Potassium Q/I relationship for El Rocío soil.

Table 31. Potassium Q/I parameters and Gapon's selectivity coefficient for the soils examined.

Soil	Exchangeable K	Exchangeable Ca+Mg	Adsorbed at equilibrium K	Adsorbed at equilibrium Ca+Mg	AR_e^K	$\Delta K°$	Kx	PBC^K	Kg
	---------meq/100g---------				$(mole/\ell)^{\frac{1}{2}}$	--meq/100g--		$\frac{(meq/100g)}{(\ell/mole)^{\frac{1}{2}}}$	(ℓ/mole)
Guanipa 1	0.08	1.80	0.13	1.92	0.0017	0.05	0.09	1.69	1.47
Guanipa 5A	0.04	0.60	0.07	0.97	0.0026	0.03	0.03	1.16	1.45
Guanipa 5B	0.02	0.30	0.08	0.58	0.009	0.02	0.03	1.30	2.70
San Cristóbal	0.50	13.60	1.43	13.65	0.003	0.24	0.26	56.40	5.50
El Rocío	0.15	3.50	0.70	4.12	0.002	0.08	0.07	17.18	5.17
Bajo Seco	0.55	7.35	0.87	7.54	0.017	0.30	0.30	14.78	2.97
Guataparo	0.25	1.42	0.46	0.98	0.017	0.16	0.07	6.19	10.15
Guanaguanare	0.19	8.10	0.60	8.58	0.003	0.11	0.09	21.56	2.25
Alambre	0.15	3.40	0.50	3.90	0.0039	0.07	0.05	9.20	3.20
El Potrero	0.30	2.10	0.67	2.50	0.008	0.16	0.04	8.26	6.86
Barinas	0.15	1.51	0.46	2.07	0.005	0.09	0.06	8.20	5.20
Red Bay A1	0.26	6.72	0.50	7.16	0.025	0.17	0.06	14.20	1.58
Red Bay B2t	0.05	0.83	0.46	0.99	0.0012	0.01	0.03	12.40	12.89

The K Q/I parameters found in Red Bay tended to decrease with depth. The decrease of K with depth in this soil and in Guanipa 5 was probably caused by fixation by the increasing clay contents in deeper horizons. Decrease of AR_e^k with depth seemed to indicate that available K depended on K adsorbed on organic matter. The ΔK^o values indicated that there was little labile K in these soils. Values for PBC^k tended to increase with depth in Guanipa 5 probably due to the effect of $CaCl_2$ in increasing pH-dependent CEC by removing substances blocking the exchange surfaces, and increasing the reactive surface participating in the Q/I exchange equilibria (Lee, 1973).

The values of K, Ca, and Mg shown in Table 31 were used to calculate the Gapon selectivity coefficient (KG) for those soils. The highest value of Ca + Mg adsorbed was shown in El Rocío soil while the Guataparo soil showed a negative adsorption (desorption) of Ca + Mg. The latter indicated a high selectivity for K. All Gapon selectivity coefficient (KG) values were larger than unity indicating a high selectivity for K, especially Guataparo and Red Bay B2t.

These results indicate that the negatively charged sites for exchange in these soils in their "natural" conditions have higher selectivities for monovalent cations. It also suggests that the charge density is low, and some soil surfaces (San Cristóbal and Bajo Seco) have specific sites to fix ions with ionic radii with sizes similar to K.

Positive Surface Charge

In order to characterize positive surface charge, several studies of P adsorption and factors affecting it were carried out. Langmuir and Freundlich isotherms were used to determine the behavior of P adsorption in these soils.

Phosphorus Adsorption

Correlation coefficients between the adsorbed P (x/m) and P concentration in soil solutions at equilibrium were significant for all soils which permitted Langmuir adsorption maxima to be calculated (Fig. 6). The data showed that at any particular final P concentration, P sorption was largest for Guanaguanare soil and least for Barinas soil (Table 32). However, the overall shape of the isotherms was remarkably similar. Each isotherm was characterized by a large change in the amount of P sorbed over a low P concentration range followed by a more gradual change in the amount of P sorbed with increasing P concentrations.

To facilitate comparison with other physical and chemical processes, K values for each soil were transformed into corresponding free energies for sorption using the relationship $\Delta G = -RT \ln K$. This relationship, which equates K with the equilibrium constant, assumes that the activity coefficients of occupied and unoccupied sites are the same (Ryden et al., 1977a).

Values of ΔG and b for each temperature obtained for each soil are given in Table 32. An interesting feature of the equilibrium data was the similarity of ΔG values for a particular temperature. The type and properties of the soils used were only reflected in the magnitude of the sorption maxima (b) obtained for the temperature used.

Data did not fit the Langmuir isotherm for all temperatures. There were deviations from linearity, and because of this, the Freundlich isotherm was used to fit data from electrolyte and temperature-effect experiments.

Temperature effects. The P adsorption isotherms were determined on all soils used in this study at 5°, 25°, and 40°C. The extent of

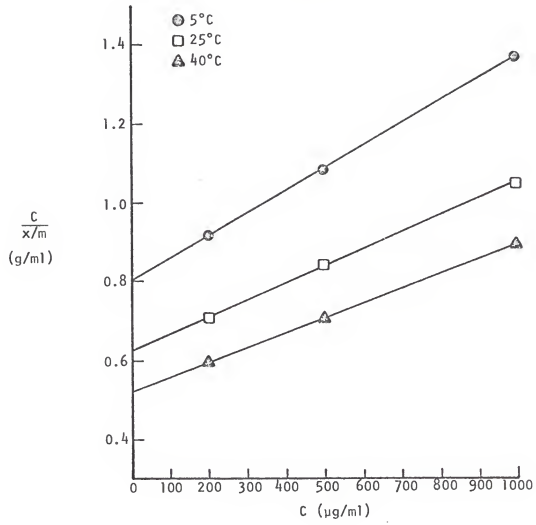

Fig. 6. Langmuir adsorption isotherms for San Cristóbal soil in non-saturated systems at three temperatures.

Table 32. Phosphorus sorption constants at different temperatures from the Langmuir equation.

Soil	ΔG_s	ΔG_{25}	ΔG_{40}†	b_5	b_{25}	b_{40}†
	------Kcal/mole--------			--------mmole/g--------		
San Cristóbal	-2.96	-3.16	-3.37	59.69	75.02	84.89
El Rocío	-3.07	-3.53	-3.43	56.59	71.68	82.71
Bajo Seco	-2.95	-3.49	-3.85	53.76	56.59	63.25
Guataparo	-2.85	-3.29	-3.46	50.56	49.63	49.63
Guanaguanare	-3.14	-3.85	-4.29	62.04	80.65	97.74
Alambre	-3.29	-3.66	-3.89	70.13	73.31	82.71
El Potrero	-3.01	-3.39	-3.53	68.64	70.13	80.65
Barinas	-2.89	-3.25	-2.99	44.19	46.75	84.89
Red Bay A1	-2.94	-3.47	-3.47	48.88	50.40	57.69
Red Bay B2t	-3.10	-3.22	-3.59	46.75	56.59	53.74

†The ΔG is the free energy of sorption from the Langmuir sorption energy constant and b is the sorption maximum.

adsorption is shown by the data from the Freundlich equation in Table 33 for selected soils. These data showed that although the values of K changed with temperature, the value of (1/n) remained similar. The constant K varied widely among soils. The values of K ranged from 10.2 to 147.9 at 5°C, from 10.7 to 199.7 at 25°C, and from 10.7 to 263.1 at 40°C. Sandy soils showed the lowest K values. The values of the exponent of the Freundlich isotherm (1/n) were in all cases between 0.33 and 0.50. The linearity of the plots of equation (2) (Fig. 7) implies that a sufficiently wide spectrum of sites existed in the total surface to satisfy the condition that the bonding energy decreased exponentially with increasing site coverage (White and Taylor, 1977). The larger values of 1/n were associated with soils having relatively fewer kinds of adsorption sites. It is possible that low values of 1/n could occur with an adsorbent containing more than one type of adsorption site (Mukhtar, 1976).

An increase in temperature increased adsorption of phosphate in these soils suggesting that greater number of new sites would become available with increasing temperature (Fig. 7 and Table 33). This indicates a strengthening of the attractive forces between the phosphate ions and the soil. One would expect the standard enthalpy associated with the adsorption process to be endothermic. These new sites were presumably formed by breaking some bonds as pointed out by Muljadi et al. (1966). The heat of adsorption may thus be divided into two parts: (a) that due to the effect of temperature on the equilibrium constant (K) of the exchange process, and (b) that due to the irreversible increase in the number of adsorption sites, i.e., an endothermic process.

Table 33. Freundlich equations for phosphorus adsorption at different temperatures for the soils examined.

Soil	5°C			25°C			40°C		
	K	$\frac{1}{n}$	R^2	K	$\frac{1}{n}$	R^2	K	$\frac{1}{n}$	R^2
Guanipa 1	10.5	0.44	0.97a†	12.0	0.50	0.96ab	14.1	0.46	0.95b
Guanipa 5A	10.2	0.50	0.97c	11.7	0.50	0.94cd	11.7	0.53	0.95d
Guanipa 5B	10.2	0.50	0.98e	10.7	0.50	0.96e	10.7	0.50	0.99e
San Cristóbal	66.1	0.47	0.98f	85.1	0.46	0.99fg	100.0	0.47	0.99g
El Rocío	83.1	0.43	0.99h	162.2	0.42	0.96hi	244.0	0.45	0.96i
Bajo Seco	95.5	0.39	0.98j	104.8	0.44	0.81jk	213.8	0.33	0.96k
Guataparo	67.6	0.43	0.98l	75.8	0.45	0.80l	93.4	0.40	0.98l
Guanaguanare	147.9	0.36	0.99m	165.9	0.44	0.88mn	263.1	0.40	0.85n
Alambre	134.9	0.41	0.99o	199.7	0.37	0.96op	240.0	0.33	0.99p
El Potrero	104.8	0.42	0.99q	109.7	0.44	0.97q	123.0	0.44	0.99q
Barinas	58.9	0.43	0.98r	77.6	0.43	0.97s	97.8	0.43	0.94t
Red Bay A1	77.6	0.42	0.99u	109.7	0.39	0.98ur	123.0	0.37	0.99v
Red Bay B2t	102.4	0.37	0.98x	123.0	0.37	0.97x	158.5	0.33	0.99x

†Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

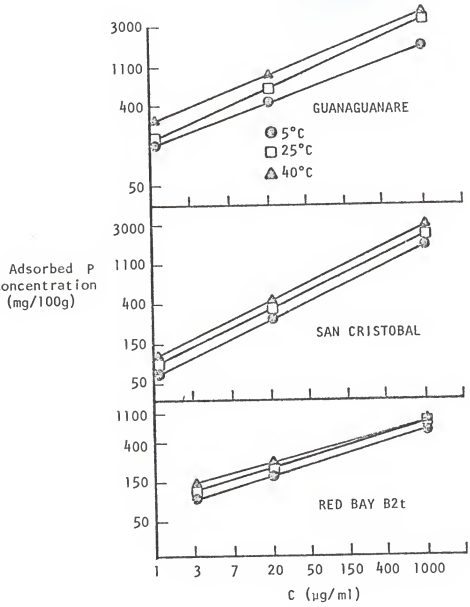

Fig. 7. Freundlich adsorption isotherms for P by Guanaguanare, San Cristóbal, and Red Bay B2t in nonsaturated systems at three temperatures.

Ionic system effects. These soils were selected to contain different proportions of particular components and to have different properties with respect to P sorption. The soils differed appreciably in their ability to sorb P from Ca-, K-, and nonsaturated systems as shown by the isotherms (Fig. 8 and Table 34). The composition and concentration of supporting media had marked effects on the amounts of P sorbed. For Guanipa 1, Guataparo, Guanaguanare, Alambre, and Barinas soils, the P adsorbed followed the order Ca > K > nonsaturated, while San Cristóbal, Bajo Seco, and El Potrero soils showed K > Ca > nonsaturated. The sequence of isotherms for El Rocío soil appeared to be somewhat different because the Ca-saturated system adsorbed more P than the nonsaturated and this more than the K-saturated system. The difference in the P sorption isotherms obtained with the three supporting media demonstrated an effect of cation species on P sorption. The high P adsorption from the K-system is related to values of ΔK° and Kx in Q/I curves shown by San Cristóbal, Bajo Seco, and El Potrero soils.

The average pH values of supernatant solutions of the various supporting media following an 11-day sorption period were higher in nonsaturated than in K-saturated and this higher than Ca-saturated system in the Guanipa 1, El Rocío, Bajo Seco, Guanaguanare, and Alambre soils while San Cristóbal, Guataparo, and El Potrero soils showed a sequence K > non- > Ca-saturated system. Furthermore, for the Barinas soil the order of decreasing pH values of the supernatant solutions of various supporting media were the same as the order of decrease in P sorption from respective support media (Table 34). This soil was the one with largest difference between pHK_2SO_4 and pHKCl; this ΔpH value has been considered to be related to the adsorption of anions in soils (Adams, 1976).

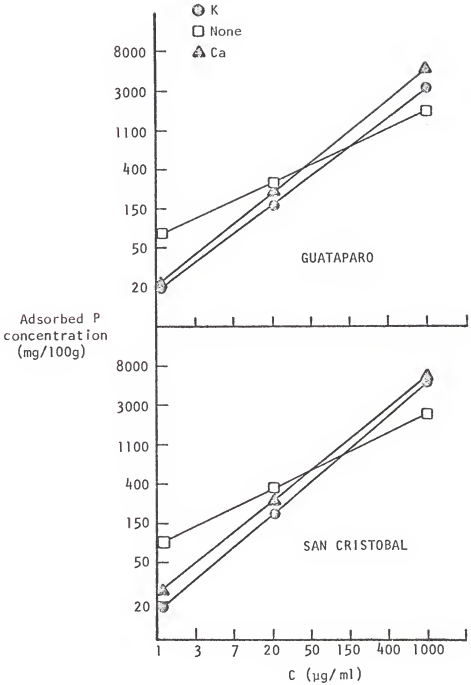

Fig. 8. Freundlich adsorption isotherms for P by Guataparo and San Cristóbal in different ionic systems at 25°C.

Table 34. Freundlich equations for phosphorus adsorption at different ionic systems for the Venezuelan soils examined.

Soil	Nonsaturated			K-saturated			Ca-saturated		
	K	$\frac{1}{n}$	R^2	K	$\frac{1}{n}$	R^2	K	$\frac{1}{n}$	R^2
Guanipa 1	12.0	0.50	0.96a†	28.7	0.47	0.52ab	29.4	0.99	0.99b
San Cristóbal	85.1	0.46	0.99c	15.1	0.86	0.91d	25.5	0.78	0.89d
El Rocío	162.2	0.42	0.96e	33.9	0.62	0.93f	29.2	0.77	0.70f
Bajo Seco	104.8	0.44	0.81g	100.5	1.38	0.89g	35.2	0.69	0.99h
Guataparo	75.8	0.45	0.80i	19.2	0.73	0.94j	20.7	0.79	0.92j
Guanaguanare	165.9	0.44	0.88k	18.1	0.77	0.97l	23.3	0.77	0.91l
Alambre	199.7	0.37	0.96m	25.5	0.74	0.93n	36.1	0.74	0.83n
El Potrero	109.7	0.44	0.97o	23.0	0.93	0.88p	32.6	0.75	0.89p
Barinas	77.6	0.43	0.97q	10.4	0.81	0.94r	47.5	0.68	0.80s

† Values within rows followed by the same letter do not differ significantly at 5% level if probability as judged by Duncan's Multiple Range test.

It has been shown (Helyar et al., 1976a) that increasing $CaCl_2$ concentration increases P adsorption. Calcium increases adsorption because it complexes with adjacent adsorbed phosphate ions, reducing the repulsion force between them. The higher effect of Ca than K on P adsorption in some of the soils suggested a specific association between Ca and the adsorbed P. In soils which contain exchangeable Ca, additions of any neutral salt displace Ca into solution. The increased Ca concentration in solution could then lead to increased P adsorption by the hydrous oxides as a result of the specific effect. Consistent with this are reports showing that the relative effect of the common cations in increasing P adsorption by soils increases in the order Na > K > Mg > Ca. This same order would be expected if the increased P adsorption were due to increased Ca added to or displaced into the solution phase (Helyar et al., 1976a). It has been suggested (Helyar et al., 1976b) that two adjacent adsorbed P ions could form a stable surface complex with a cation if it were divalent, if it were able to form a coordinate bond with two pairs of resonant 0.5^- charge oxygen atoms in one plane, and if it had a radius of about 1 Å.

The higher adsorption of P in K-systems in some soils was probably due to the high capacity of those soils to fix K and a probable occlusion or adsorption of K phosphate, e.g., $(K^+H_2PO_4^-)$ into an amorphous or semi-crystalline region of the clay surface as pointed out by Barrow and Shaw (1975b).

Thermodynamic parameters associated with adsorption process. Thermodynamic parameters are thought to be related to bonding energies and can be useful in determining mechanisms of adsorption. Enthalpy (ΔH) is heat content and is an extensive state property. It represents the amount of heat evolved in the adsorption of a definitive quantity of solute on an

adsorbent. The bonding energy is stronger as the value of H is more negative. The symbol G is a property of the state and is called free energy of the system or Gibbs free energy. The value ΔG gives an idea about equilibrium conditions. If $\Delta G = 0$, the system is at equilibrium, while if ΔG is negative the process tends to proceed. A positive value of ΔG means that the reaction tends to reverse. Also, another quantity called the entropy change (ΔS) as been found to affect the equilibrium constant of a reaction. The entropy change is an extensive property of the system. If entropy is less than zero, the cycle of any reaction will be reversible (Adamson, 1976; Biggar and Cheung, 1973; Mukhtar, 1976).

Thermodynamics of P adsorption were calculated using Freundlich equation for the sorption of P, the equilibrium constants obtained from the relationship between solution P concentration and reciprocal of time, and Biggar and Cheung (1973) methods. The values of ΔG, ΔH, and ΔS are shown in Tables 35, 36, and 37. The limitations of these calculations are that no acceptable method of defining and measuring the activity coefficient (used in G calculations) in adsorbed liquid phase has been developed.

The ΔG values calculated using the K value obtained from plots of concentration of P solutions against the reciprocal of the time at 25°C are shown in Table 35 and Fig. 9. The ΔG values were negative for all soils and ranged from -1.39 to -3.52 Kcal/mole. The values of ΔG obtained were all negative ranging from -1.29 to -3.45 Kcal/mole for temperatures ranging from 5° to 40°C (Table 36). These values correlated well with those found from the equilibrium concentration-reciprocal time relationship at 25°C. The ΔH and ΔS values were positive. The

Table 35. Equations of the relationship between solution phosphorus concentration and reciprocal of time, and the K and ΔG values calculated from the concentration at equilibrium for the soils examined.

Soil	Equation	R^2	K	ΔG
			ℓ/mole	Kcal/mole
Guanipa 1	$C = 42.84 + 3.09\ t_{-1}^{-1}$	0.82	5.16	-0.90
Guanipa 5A	$C = 42.25 + 2.04\ t_{-1}^{-1}$	0.92	3.26	-0.65
Guanipa 5B	$C = 43.65 + 5.04\ t_{-1}^{-1}$	0.85	45.11	-2.10
San Cristóbal	$C = 18.66 + 5.19\ t_{-1}^{-1}$	0.82	52.05	-2.17
El Rocío	$C = 22.41 + 5.54\ t_{-1}^{-1}$	0.83	38.16	-2.00
Bajo Seco	$C = 29.58 + 7.22\ t_{-1}^{-1}$	0.81	21.39	-1.68
Guataparo	$C = 24.11 + 9.48\ t_{-1}^{-1}$	0.91	33.26	-1.93
Guanaguanare	$C = 27.12 + 7.23\ t_{-1}^{-1}$	0.88	26.13	-1.79
Alambre	$C = 10.00 + 6.19\ t_{-1}^{-1}$	0.81	124.0	-2.65
El Potrero	$C = 15.20 + 6.97\ t_{-1}^{-1}$	0.80	70.96	-2.34
Barinas	$C = 25.31 + 5.98\ t_{-1}^{-1}$	0.80	30.23	-1.88
Red Bay A1	$C = 21.72 + 16.16\ t_{-1}^{-1}$	0.84	30.35	-1.88
Red Bay B2t	$C = 16.56 + 6.40\ t^{-1}$	0.83	62.59	-2.28

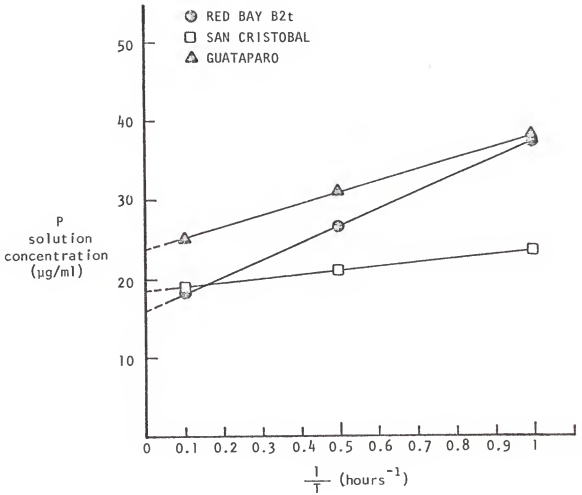

Fig. 9. Relationship between P solution concentration and the reciprocal of time for Guataparo, San Cristóbal, and Red Bay B2t soils.

Table 36. Thermodynamic parameters calculated using Freundlich equations for phosphorus adsorption reactions for the soils examined.

Soil	ΔG_5	ΔG_{25}	ΔG_{40}+	ΔH	ΔS_5	ΔS_{25}	ΔS_{40}
	----------Kcal/mole----------				------cal/mole°K-------		
Guanipa 1	-1.30	-1.47	-1.64	1.45	9.89	9.80	9.87
Guanipa 5A	-1.29	-1.45	-1.52	1.13	8.71	8.66	8.47
Guanipa 5B	-1.29	-1.41	-1.48	0.23	5.47	5.50	5.46
San Cristóbal	-2.31	-2.63	-2.86	2.05	15.68	15.70	15.69
El Rocío	-2.43	-2.99	-3.36	4.93	26.47	26.58	26.58
Bajo Seco	-2.51	-2.74	-3.32	3.73	22.45	21.71	22.52
Guataparo	-2.32	-2.56	-2.81	1.54	13.88	13.76	13.90
Guanaguanare	-2.75	-3.02	-3.45	2.69	19.57	19.16	19.62
Alambre	-2.70	-3.13	-3.41	2.85	19.96	20.07	20.00
El Potrero	-2.56	-2.76	-2.99	0.76	11.94	11.81	11.98
Barinas	-2.24	-2.58	-2.83	2.46	16.91	16.91	16.90
Red Bay A1	-2.40	-2.76	-2.94	2.30	16.91	16.98	16.74
Red Bay B2t	-2.50	-2.83	-3.13	2.09	16.51	16.51	16.68

+The subscripts (5, 25, and 40) indicate the isotherm temperatures 5, 25, and 40°C.

Table 37. Values of K°, ΔG°, ΔH°, and ΔS° associated with the adsorption of phosphorus for the selected soils calculated by the Biggar and Cheung method (1973).

Soil	K°			ΔG°			ΔH°	ΔS°		
	5°C	25°C	40°C	5°C	25°C	40°C		5°C	25°C	40°C
				-----Kcal/mole------				------cal/mole°K-------		
Guanipa 1	1.17	1.20	1.54	0.09	0.11	0.27	1.24	4.78	4.53	4.82
San Cristóbal	1.06	1.26	1.57	0.03	0.23	0.28	1.86	6.80	6.70	6.84
El Rocío	1.75	2.12	2.64	0.31	0.44	0.60	1.91	7.99	7.90	8.02
Bajo Seco	1.51	1.84	4.85	0.23	0.36	0.98	5.46	20.46	19.53	20.58
Guanaguanare	2.18	2.25	2.03	0.43	0.48	0.86	2.96	12.19	11.54	12.20
Guataparo	1.58	1.84	4.01	0.25	0.36	0.44	1.23	5.32	5.30	5.34
Alambre	2.46	3.22	3.29	0.49	0.69	0.74	1.49	7.12	7.32	7.12
El Potrero	1.20	1.48	1.70	0.10	0.23	0.33	1.73	6.58	6.58	6.58
Barinas	1.45	1.48	1.49	0.21	0.23	0.25	0.12	1.17	1.17	1.18
Red Bay A1	2.44	3.32	4.48	0.49	0.71	0.93	3.11	12.95	12.82	12.90
Red Bay B2t	1.12	2.20	3.49	0.06	0.47	0.78	5.68	20.64	20.64	20.64

values of Ko, $\Delta G°$, $\Delta H°$, and $\Delta S°$ (Table 37) associated with the adsorption were calculated, respectively, according to equations (5), (9), (10), and (11) (Biggar and Cheung, 1973). Values of $\Delta H°$ were calculated from plots of ln K vs 1/T. The linear nature of the plot indicated that the mechanism of adsorption did not change as temperature was changed. The amount of adsorption was changed because the supply of thermal energy was different. The $\Delta G°$ values were in the range of -0.03 to -0.98 Kcal/mole between temperatures 5° and 40°C. The negative values of $\Delta G°$ indicated adsorption processes which were expected because of the reported fixation of P in these soils. The ΔG values are related to the amount of P adsorbed. It can be observed in Tables 35, 36, and 37 that soils with higher values of ΔG (more negative) adsorbed more phosphate. Even though the values in Table 35 have the limitation mentioned before, it was clear that the lower the equilibrium concentration the more negative the ΔG values. If one examines the thermodynamic parameters as contained in Table 37, one notices that $\Delta H°$ and $\Delta S°$ for the adsorption process with the different soils ranged from 0.12 to 5.68 Kcal/mole and 1.17 to 20.64 cal/mole degree. The drastic differences in $\Delta H°$ and $\Delta S°$ values indicated different adsorption mechanisms. Also, change in free energy is related to adsorption energy; the more negative the $\Delta G°$ the greater is thought to be the bonding strength. Thus, it is correlated with mechanisms of adsorption (Mukhtar, 1976).

The positive values of ΔS in phosphate may be the result of replacing more ordered water molecules which may be adsorbed on the surface in a less orderly fashion (more entropy), and consequently gives a positive entropy change. A positive entropy change is also commonly observed in formation of a complex where a ligand displaces several

water molecules from around a central ion (Muljadi et al., 1966). The positive entropy change observed for the phosphate adsorption may be attributed to a disordering of water molecules around the adsorbing site and the adsorbate. Muljadi et al. (1966) suggested that the adsorption of one mole of phosphate corresponded to the liberation of about 2 moles of water. The high positive value of ΔS in these soils may be related to the P fixation on Fe oxides. Bajo Seco, Guanaguanare, and Red Bay soils showed the highest values of ΔS (Table 37) and from P fractionation data (Tables 7 through 19), these soils showed a tendency to fix more P as Fe than as Al. This P fixation by Fe and also the contribution of Al compounds increases the amount of water displaced from the soil surface (Muljadi et al., 1966). These results agree with Ryden et al. (1977a) who proposed a mechanism for three regions. During P adsorption the surface becomes negatively charged because P adsorption involves potential determining mechanisms. The portion of surface active in P adsorption may be represented as a series of single coordinated -OH groups, some of which may be protonated. The proportion of $-OH_2$ to -OH is determined, among other factors, by the pH and PZNC of the surface (Ryden et al., 1977a).

It is clear that there is more than one type of interaction site on the soil surfaces. The interaction process of the phosphate ions with the soil usually involves more than one mechanism depending on the physical and chemical properties of the soil, its major clay minerals constituents, the experimental condition, and the concentration of P (Mukhtar, 1976). However, a single mechanism may dominate.

The above results suggested that in these tropical soils phosphate ions are bonded to positive charge in Al and Fe compounds by displacement of $-OH_2$ and -OH groups and that in some soils (Guanaguanare,

Bajo Seco, and Red Bay), the contribution of Fe oxides to P adsorption was larger than in the others.

Phosphorus Release

In Table 38 and Fig. 10 the values of P release after adsorption equilibrium are shown as related to the number of washings for the Venezuelan soils at the highest P application. Values of b_1 and a from the equation $Y = b_1 - aX$ are shown, where Y = the accumulative P desorbed or released, and X = the number of washing, b_1 = the intercept, and a = the slope of the straight line, when ln Y is plotted against X.

The data show that the amount of P released was quite different in each soil and the order of P release in the different ionic system varied with soils. In Barinas and Guanaguanare soils, the sequence of P released was K- > Ca- > nonsaturated system, while in Alambre and Guataparo soils, it was Ca- > non- > K-saturated. On the other hand, El Potrero and Bajo Seco showed a non- > Ca- > K-saturated system sequence. The sequence in San Cristóbal and El Rocío soils was non- > K- > Ca-saturated system, while Guanipa showed a very different sequence, K- non- > Ca-saturated system. The P released tended to be the same in each additional washing. The linear nature of the plot of the ln Y vs X indicated that the release of P becomes asymptotic with the number of washings. This behavior of soils with respect to P liberation is related to the strength of adsorption and the specific effect of each cation. Those soils with mineralogical composition that increase K adsorption like Alambre, Guataparo, Bajo Seco, and El Potrero showed a low release of P into the K system. While those soils where the P was associated with Ca showed a low release into Ca systems. In Guanaguanare and

Table 38. Relationship between the accumulative released P and the number of washings and linear correlation coefficients for the Venezuelan soils with different ionic systems.

Soil	Nonsaturated				K saturated				Ca saturated			
	P adsorbed	b	a	r	P adsorbed	b	a	r	P adsorbed	b	a	r
Guanipa 1	51.2	5.02	0.09	0.90	77.7	5.40	0.08	0.94	191.8	3.66	0.12	0.97
San Cristóbal	228.2	6.67	0.11	0.92	371.2	5.34	0.11	0.86	340.5	3.66	0.27	0.91
El Rocío	256.4	5.40	0.15	0.92	138.8	5.49	0.13	0.94	346.3	4.45	0.21	0.91
Bajo Seco	208.5	7.03	0.05	0.93	225.0	5.92	0.11	0.88	360.3	5.15	0.19	0.82
Guataparo	202.4	6.20	0.07	0.94	180.6	5.19	0.13	0.91	364.2	6.94	0.04	0.94
Guanaguanare	223.6	4.94	0.21	0.91	259.3	6.38	0.08	0.92	340.5	6.47	0.06	0.96
Alambre	214.7	5.45	0.16	0.95	233.7	5.86	0.11	0.91	347.0	6.59	0.09	0.94
El Potrero	205.2	5.93	0.15	0.90	225.0	5.14	0.12	0.95	326.8	5.74	0.14	0.87
Barinas	138.4	5.67	0.14	0.91	180.6	7.18	0.04	0.94	342.4	6.36	0.08	0.94

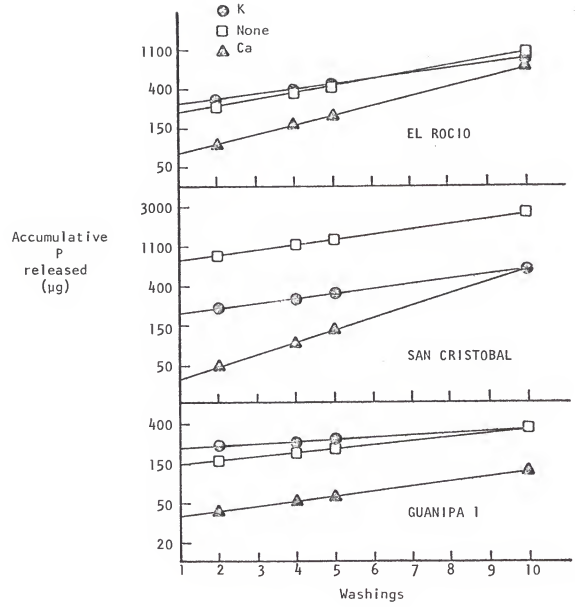

Fig. 10. Release of phosphorus from Guanipa 1, San Cristóbal, and El Rocío soils.

Barinas soils, saturation with K and Ca increased P release which may have been caused by reduction in P bonding strength to Al and Fe (Table 38).

Changes in Charge Surface

The increase of negative charge in soils with lime is known and has been attributed to ionization of organic matter groups and OH groups attached to Si of broken tetrahedral positions (Wiklander, 1967). On the other hand, the increase in negative charge with P adsorption has been attributed to the replacement of hydroxyl ions by phosphate at the surface of clay minerals and sesquioxides (Sawhney, 1974). Lime and P effects on CEC together with cropping effect on this "new" CEC are discussed in the following paragraphs.

Lime and Phosphorus Effects

Guanipa 1, Guanipa 5, and El Potrero soils were selected to determine the effects of combination of P and $CaCO_3$ on soil reactivity before and after cropping. Sorghum (Sorghum bicolor L.) was chosen to measure the effects of $CaCO_3$ and P on dry matter yields and at the same time to observe the effect of cropping on changes in pH, PZNC, and CEC of soils treated with $CaCO_3$ and P.

The effects of $CaCO_3$ and P treatments on pH, PZNC, and CEC before cropping were as expected (Tables 39, 40, and 41). There was a highly significant effect of $CaCO_3$ on pH increase due to the neutralization of exchangeable Al. On the other hand, the adsorption of P decreased the PZNC due to the neutralization of positive charge and to the reversion of charge by the negative charge of the phosphate anions. Calcium

Table 39. Effect of treatments on electrochemical properties measured before cropping for the Guanipa 1 soil.

Treatment	pH	PZNC	EC	CEC
			mmhos/cm	meq/100g
12	6.20b[+]	3.70ab	0.83c	5.64c
13	6.28b	3.60b	1.08abc	6.46b
14	6.35b	3.55b	1.44abc	7.03b
22	6.25b	3.80ab	0.88abc	5.41c
23	6.50a	3.50b	1.06abc	8.02ab
24	6.50a	2.30c	1.30abc	17.65ab
32	6.28b	3.50b	0.63bc	6.94b
33	6.35b	3.40b	1.33abc	7.77ab
34	6.60a	3.30b	1.01abc	9.70a
42	6.25b	3.50b	0.80abc	6.79b
43	6.40b	4.00a	1.06abc	5.18c
44	6.60a	4.10a	1.16a	5.64c

[+]Values within rows followed by the same letter do not differ significantly at 5% level if probability as judged by Duncan's Multiple Range test.

Table 40. Effect of treatments on electrochemical properties measured before cropping for the Guanipa 5 soil.

Treatment	pH	PZNC	EC	CEC
			mmhos/cm	meq/100g
12	5.60ab[+]	3.90a	0.48c	2.15c
13	5.50ab	3.65b	0.59c	2.65c
14	5.80ab	3.60b	0.95b	3.99c
22	5.68ab	4.00a	0.55c	2.09c
23	5.55ab	3.70b	0.64c	2.65c
24	5.90a	2.50c	1.05b	9.62a
32	5.53ab	3.70b	0.40c	2.58c
33	5.98a	3.60a	0.75bc	4.74b
34	6.05ab	3.50b	1.25a	5.46b
42	5.53ab	3.70b	0.53c	2.58c
43	5.60ab	3.50b	0.59c	3.59c
44	5.98a	3.90a	1.50a	3.51c

[+]Values within rows followed by the same letter do not differ significantly at 5% level if probability as judged by Duncan's Multiple Range test.

Table 41. Effect of treatments on electrochemical properties measured before cropping for the El Potrero soil.

Treatment	pH	PZNC	EC	CEC
			mmhos/cm	meq/100g
12	4.65 d[+]	3.20 b	0.78 c	38.27 d
13	4.70 d	3.00 b	1.00 c	55.87 c
14	4.95 d	3.00 b	1.81 ab	78.06 b
22	4.88 d	3.40 b	1.06	40.13 a
23	5.03 d	3.15 b	1.49 b	71.44 bc
24	5.28 c	2.90 c	2.44 a	122.85 a
32	5.20 c	3.25 b	1.13 c	78.06 b
33	5.25 c	3.80 ab	1.56 b	38.27 d
34	5.55 bc	3.80 ab	2.13 a	59.97 c
42	6.20 a	3.50 ab	1.14 c	158.15 a
43	5.95 b	4.20 a	2.75 a	59.97 c
44	6.18 a	4.30 a	2.38 a	71.44 bc

[+]Values within rows followed by the same letter do not differ significantly at 5% level if probability as judged by Duncan's Multiple Range test.

carbonate treatments at high levels increased PZNC. This was probably caused by precipitation of calcium phosphate and also to the effect of Ca on the exchange complex. Divalent specifically adsorbed cations increase the PZNC of colloids with constant potential surface and, therefore, decrease CEC (Breewsman, 1973; Adams, 1976). In these soils, the combined effect of decreased PZNC and increased pH brought about an increase in CEC as calculated by the Van Raij and Peech method (1972).

The effect of $CaCO_3$ and P treatments before cropping were not so marked as after cropping perhaps due to the shorter time of contact and also to an enhancement of reactions by the crop.

The effect of combination levels of P and $CaCO_3$ on pH, PZNC, Gouy-Chapman and Stern potentials, and the distribution of charge on the surface for the selected soils after cropping were calculated using Van Raij and Peech procedure (1972) (Tables 42 through 50). The variables examined showed differences among soils. The pH increased with increasing levels of $CaCO_3$ and P. The values of PZNC were changed significantly by increasing levels of P. The PZNC decreased with P levels at low levels of $CaCO_3$, but increased at high levels. The effect of P on pH values may have been caused by exchange of phosphate with OH groups (Rajan, 1978). The effect of P on PZNC has been attributed to the increase in negative charge. The increase of PZNC with phosphate application at higher levels of $CaCO_3$ was probably due to a precipitation of Ca phosphate compounds.

The Stern potential is the electric potential at the boundary between the Stern layer and the diffuse layer. The Gouy-Chapman potential is the electric potential at the boundary between diffuse layer and bulk solution. The values of Stern potential are used to calculate the charge

Table 42. pH and point of zero net charge for $CaCO_3$ and phosphorus treatments in Guanipa l after cropping.

Treatment combination	pH	PZNC
11	5.52def[+]	4.05a
12	5.50def	3.40b
13	5.73bcde	3.35b
14	5.97abc	3.40ab
21	5.52def	3.65a
22	5.68cde	3.35b
23	5.71cde	3.10b
24	6.23a	3.35ab
31	5.42ef	3.30a
32	5.68cde	3.55b
33	6.00abc	3.90b
34	6.07ab	3.65ab
41	5.22f	3.80a
42	5.65cde	3.00b
43	5.60ed	3.70b
44	5.80bcd	3.55ab

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 43. pH and point of zero net charge for $CaCO_3$ and phosphorus treatments in Guanipa 5 after cropping.

Treatment combination	pH	PZNC
11	5.37c[+]	3.90a
12	5.32c	3.60b
13	5.52c	3.60b
14	6.72a	3.50ab
21	5.47c	3.90a
22	5.40c	3.25b
23	5.60bc	3.35b
24	6.87a	3.90ab
31	5.62bc	3.87a
32	5.37c	3.15b
33	5.87b	3.55b
34	6.80a	3.75ab
41	5.43c	3.60a
42	5.38c	3.55b
43	5.48c	3.35b
44	6.70a	3.95ab

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 44. pH and point of zero net charge for $CaCO_3$ and phosphorus treatments in El Potrero after cropping.

Treatment combination	pH	PZNC
11	4.25h[+]	3.50a
12	4.70f	3.05b
13	4.70f	3.00b
14	5.00e	2.60b
21	4.48g	3.60a
22	5.07de	3.10b
23	5.12de	3.25b
24	5.43c	3.55ab
31	4.77f	3.50a
32	5.19de	3.05b
33	5.23d	3.65b
34	5.75b	3.80ab
41	5.72b	4.30a
42	5.98a	4.20a
43	5.97a	3.45b
44	6.02a	3.55ab

[+]Values within rows followed by the same letter do not differ signifcantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 45. Electrochemical potentials of $CaCO_3$ and phosphorus treatments in soil Guanipa 1 after cropping.

Treatment combination	GC potential	Stern potential
	----------Volts----------	
11	0.087g[+]	0.086
12	0.124	0.123
13	0.141bcd	0.139
14	0.151abc	0.150
21	0.110	0.109
22	0.138bcd	0.137
23	0.154ab	0.152
24	0.170a	0.168
31	0.125edf	0.124
32	0.126edf	0.125
33	0.124edf	0.123
34	0.143bcd	0.141
41	0.084g	0.083
42	0.156ab	0.155
43	0.112ef	0.111
44	0.133cde	0.132

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 46. Electrochemical potentials of $CaCO_3$ and phosphorus treatments in soil Guanipa 5 after cropping.

Treatment combination	GC potential	Stern potential
	----------Volts----------	
11	0.106	0.105cdef[+]
12	0.100	0.100ef
13	0.113	0.112bcdef
14	0.170	0.168a
21	0.093	0.092f
22	0.127	0.126bcde
23	0.133	0.132bc
24	0.175	0.173a
31	0.103	0.103def
32	0.131	0.130cbd
33	0.137	0.135b
34	0.180	0.177a
41	0.108	0.108bcdef
42	0.108	0.108bcdef
43	0.126	0.125bcde
44	0.164	0.162a

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 47. Electrochemical potentials of $CaCO_3$ and phosphorus treatments in soil El Potrero after cropping.

Treatment combination	GC potential	Stern potential
	----------Volts----------	
11	0.044	0.044h[+]
12	0.097	0.097e
13	0.100	0.100de
14	0.142	0.140a
21	0.052	0.052h
22	0.116	0.115bc
23	0.110	0.109cd
24	0.111	0.110cd
31	0.075	0.074g
32	0.126	0.125b
33	0.093	0.093
34	0.115	0.114bc
41	0.084	0.083fg
42	0.105	0.105cde
43	0.148	0.147a
44	0.146	0.144a

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 48. Charge distribution at the surface for $CaCO_3$ and phosphorus treatments in Guanipa 1 after cropping.

Treatment combination	σ_1	σ_2	σ
	meq/100g		
11	0.93	0.61	0.62fg[+]
12	2.32	1.27	1.29dc
13	2.97	1.80	1.85bcd
14	3.33	2.21	2.28abc
21	1.75	0.98	0.99efg
22	2.88	1.67	1.71bcd
23	3.45	2.26	2.33ab
24	3.83	3.11	3.24a
31	2.36	1.32	1.34de
32	2.40	1.34	1.37de
33	2.31	1.31	1.34de
34	3.05	1.85	1.90bcd
41	0.83	0.57	0.57g
42	3.42	2.52	2.63ab
43	1.83	1.01	1.03
44	2.69	1.52	1.55cde

[+] Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 49. Charge distribution at the surface for $CaCO_3$ and phosphorus treatments in Guanipa 5A after cropping.

Treatment combination	σ_1	σ_2	σ
	----------meq/100g----------		
11	1.80	1.14	1.16bcde[+]
12	1.47	0.86	0.87de
13	2.02	1.13	1.15bcde
14	3.96	3.60	3.79a
21	1.19	0.74	0.75e
22	2.63	1.45	1.48bcd
23	2.88	1.64	1.68bc
24	4.24	3.66	3.83a
31	1.62	0.93	0.95cde
32	2.80	1.57	1.60bcd
33	3.00	1.84	1.89b
34	4.32	3.97	4.18a
41	1.79	1.01	1.02bcde
42	1.78	1.00	1.02bcde
43	2.58	1.42	1.45bcde
44	3.94	3.04	3.17a

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan;s Multiple Range test.

Table 50. Charge distribution at the surface for $CaCO_3$ and phosphorus treatments in El Potrero after cropping.

Treatment combination	σ_1	σ_2	σ
	meq/100g		
11	5.58	5.88	5.91h[+]
12	32.65	19.57	19.78def
13	35.24	20.70	20.93def
14	78.71	46.32	47.46a
21	7.50	7.26	7.30h
22	51.44	28.25	28.67bc
23	45.11	25.18	25.52cd
24	46.18	25.70	26.05cd
31	16.28	12.20	12.29gh
32	62.74	34.47	35.10b
33	29.07	18.00	18.18efg
34	50.45	27.91	28.33bc
41	21.90	14.80	14.92fg
42	40.01	22.82	23.10cde
43	84.95	52.85	54.33a
44	80.46	52.42	54.01a

[+]Values within rows followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan;s Multiple Range test.

in Stern layer and diffuse layer as outlined by Van Raij and Peech (1972), while the Gouy-Chapman potential is used to calculate the charge on the surface (equation 14). This model presents difficulties and is not adequate to describe realistically the relationship between the surface charge and the surface potential at high surface potential values. It was used in this study because the potential surface values were low, and this model could apply to these soil surfaces. Gouy-Chapman and Stern potentials, increased with increasing P levels and these effects were highly significant. Calculations of CEC and the charge in σ_1 and σ_2 are somewhat complicated and equations (16), (17), (18), and (19) were used. The value taken for N_1 was $10^{15} cm^{-2}$. The value of δ/ϵ^1 was 0.15 Å which was found by Van Raij and Peech (1972) to give the best fit of their experimental results; specific adsorption of ions was assumed to be negligible, thus $\phi = 0$. These substitutions finally yielded four equations with four unknowns. The solution was found by using the computer program described in Appendix III.

Even though there was an increase in the Stern-layer charge (σ_1) and diffuse-layer charge (σ_2), the effects of $CaCO_3$ levels were not significant. Munns and Fox (1977), working with an Oxisol, found that the CEC (sum of exchangeable cations) increased three fold as the pH increased, and this additional charge was almost equivalent to the amount of $CaCO_3$ reacted. On the other hand, P levels had a highly significant effect on increased charge.

The Gouy-Chapman model showed values similar to the Stern model. It seems that the potential values on these surface are low enough to allow the Gouy-Chapman model to apply. The combination of increasing pH and decreasing PZNC resulted in an increase in CEC in all soils.

The changes in soil CEC with increasing pH have been attributed to the pH-dependent CEC. Soil reactions contributing to this CEC are organic matter and clays with noncrystalline components and interlayered Al (Fiskell and Zelazny, 1971). In El Potrero soil, this increase should be greater than in the other two soils because of higher organic matter and clay contents.

Increased CEC with phosphate ions can be attributed to the replacement of hydroxyl ions by phosphate ions on the surfaces of clay minerals and sesquioxides in soils with pH 5 to 6. In soils, with lower pH values, a portion of the surface hydroxyls are protonated to form water molecules. The replacement of water molecules by phosphate ions also increases CEC (Breewsma, 1973; Mekaru and Uehara, 1972; Sawhney, 1974).

The increasing levels of P had a highly significant effect on electrical conductivity (EC). The values of EC increased with increasing P. In El Potrero soil, the EC reached values greater than 2 mmhos/cm at 25°C in the saturation extract; this is considered the limit of salinity tolerance for some crops (Hasan et al., 1970).

Effects of Change of Charge Characteristics on Crop Production

There were significant differences among soils in sorghum dry matter yields (Tables 51, 52, and 53). El Potrero had higher yields than Guanipa 1 and Guanipa 5. The latter soils did not differ in their effect on dry matter yield. Levels of $CaCO_3$ did not significantly affect dry matter yield. But, yields were increased significantly by increasing levels of applied P. On the other hand, dry matter production decreased with increasing salinity levels in soils. The decrease in dry matter production probably resulted from the decreasing availability of soil water and decreased uptake of nutrients by the crop,especially Ca and Mg associated with increasing salinity (Hasan et al., 1970).

Table 51. Dry matter yields of sorghum and cation exchange capacity after cropping for soil Guanipa 1 treated with $CaCO_3$ and phosphorus.

P applied as KH_2PO_4	$CaCO_3$ applied			
	1	2	3	4
	Oven-dry plant material, g/pot			
1	1.12b[+]	1.02b	0.92b	1.12b
2	3.23a	3.28a	3.01a	3.21a
3	3.41a	3.25a	2.94a	3.74a
4	2.97a	3.10a	3.08a	3.44a
	CEC, meq/100g			
1	1.54fg	2.72efg	3.68de	1.40g
2	3.59dc	4.55bcd	3.74de	5.94ab
3	4.77bcd	5.71ab	3.62de	2.84ef
4	5.55abc	6.94a	4.91bcd	4.21cde

[+]Values within subtables followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 52. Dry matter yields of sorghum and cation exchange capacity after cropping for soil Guanipa 5 treated with $CaCO_3$ and phosphorus.

P applied as KH_2PO_4	$CaCO_3$ applied			
	1	2	3	4
	Oven-dry plant material, g/pot			
1	1.08e[+]	1.05e	0.87ef	1.01e
2	3.87ab	4.19a	3.74ab	3.73ab
3	2.86bcd	2.97cd	2.62d	3.30bc
4	0.33fg	0.24fg	0.35fg	0.50efg
	CEC, meq/100g			
1	2.94bcde	1.93e	2.56bcde	2.79bcde
2	2.33de	4.08bcd	4.37bcd	2.79bcde
3	3.15bcde	4.52bc	4.84b	4.01bcde
4	7.56a	7.89a	8.29a	6.98a

[+]Values within subtables followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range Test.

Table 53. Dry matter yields of sorghum and cation exchange capacity after cropping for soil El Potrero treated with $CaCO_3$ and phosphorus.

P applied as KH_2PO_4	$CaCO_3$ applied			
	1	2	3	4
	Open-dry plant material, g/pot			
1	0.33e[+]	0.83e	0.82e	0.76e
2	2.50d	3.76abc	4.02ab	3.71abc
3	3.23bcd	3.69abc	4.26a	4.19a
4	2.94cd	3.29bcd	3.17cd	3.12cd
	CEC, meq/100g			
1	11.47i	14.76i	28.48gh	36.69fg
2	52.22def	79.69bc	97.21b	62.83cde
3	55.94def	70.29cd	47.08efg	137.80a
4	125.03a	71.88cd	78.36bc	132.87a

[+]Values within subtables followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 54. Effect of cropping on CEC values for Guanipa 5 soil.

Treatment combinations	CEC		
	Before cropping	After cropping	Difference
	----------meq/100g----------		
12	5.64	2.33	3.31b
13	4.46	3.15	1.31c
14	7.03	7.55	-0.52d
22	5.41	4.08	1.33c
23	8.02	4.52	3.50b
24	17.65	7.89	9.76a
32	6.93	4.37	2.56bc
33	7.76	4.84	2.92bc
34	9.70	8.28	1.41c
42	6.79	2.79	4.00b
43	5.18	4.00	1.18c
44	5.64	6.98	-1.34c

+Values followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 55. Effect of cropping on CEC values for Guanipa 1 soil.

Treatment combinations	CEC		
	Before cropping	After cropping	Difference
	meq/100g		
12	2.15	3.59	-1.44c[+]
13	2.65	4.77	-2.12b
14	3.99	5.54	-1.55c
22	2.09	4.55	-2.46b
23	2.65	5.70	-3.05a
24	9.62	6.94	-2.68b
32	2.58	3.74	-1.16c
33	4.74	3.62	1.12c
34	5.46	4.90	0.56d
42	2.58	5.94	-3.35a
43	3.59	2.84	0.75d
44	3.51	4.20	-0.69d

[+] Values followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 56. Effect of cropping on CEC values for El Potrero soil.

Treatment combinations	CEC		
	Before cropping	After cropping	Difference
	meq/100g		
12	38.27	52.22	-13.95b[+]
13	55.87	55.93	- 0.06a
14	78.06	125.08	-46.97a
22	40.13	79.69	-39.56a
23	71.44	70.29	+ 1.15e
24	122.85	71.87	+50.98f
32	78.06	97.21	-19.15b
33	38.27	47.07	- 8.80c
34	59.97	78.35	-18.38b
42	158.15	62.86	+95.32g
43	59.97	137.79	-77.82a
44	71.44	132.88	-61.44a

[+]Values followed by the same letter do not differ significantly at 5% level of probability as judged by Duncan's Multiple Range test.

Table 57. Change in CEC after cropping for the soils selected.

Treatment	Guanipa 1	Guanipa 5A	El Potrero
	----------meq/100g----------		
12	-1.44	3.37	-13.95
13	-2.12	1.31	- 0.06
14	-1.55	-0.52	-46.97
22	-2.46	1.33	-39.56
23	-3.05	3.50	+ 1.15
24	-2.68	9.76	+50.98
32	-1.16	2.56	-19.15
33	+1.12	2.92	- 8.80
34	+0.56	1.41	-18.38
42	-3.35	4.00	+95.32
43	+0.75	1.18	-77.82
44	+0.69	-1.34	-61.44

The most important feature of crop effect was the comparison of CEC values after cropping with those before cropping. In Tables 54 through 57, differences in CEC obtained by substracting CEC after cropping from that before cropping are shown. There were no significant differences within these values among the three soils.

The difference in CEC for Guanipa 1 soil was positive and not significant. These differences were probably due to a release of P and to decreased pH as consequence of Ca uptake by the crop. In this soil, treatments 14 and 44 with the highest level of P and the lowest and highest levels of Ca, respectively, showed an increase in CEC following cropping. This was probably due to an increase of P fixation with time at the high P concentration. Guanipa 5 soil showed negative differences of CEC except for treatment combinations 33, 34, and 43. The negative values can be explained as before to an increase in P fixation with time. The positive values may also have been due to the formation of calcium phosphate compounds that reduced PZNC because of neutralization of negative charges. As pointed out by Helyar et al. (1976a), the application of $CaCO_3$ should reduce the availability of P in soils in which phosphate is controlled by adsorption on minerals which behave like gibbsite. They may include kaolinite as well as X-ray amorphous and crystalline hydrous oxides of Fe and Al. El Potrero soil which showed a different tendency may have been due to the higher contents of organic matter, clay, and Al and Fe oxides. Three treatment combinations (23, 24, and 42) showed positive values while other treatments showed negative values. This decrease in CEC was related to the increase of PZNC caused by precipitation of Ca phosphates in this soil. This suggested that, even though the effect of $CaCO_3$ on PZNC was not significant, it had a specific effect on P adsorption and on PZNC.

In general, there seemed to be an effect of cropping in decreasing the "new" CEC obtained with $CaCO_3$ and P treatments. The treatment combinations which increased dry matter production were those that showed less CEC (Tables 54 through 57). This may have been due to the uptake of P and Ca by plants. Uptake of P by the crop leaves positive charge on the surface that canceled negative charge and decreased CEC.

The effects of soils, $CaCO_3$, P, and the interaction of $CaCO_3$ with P on the variables measured are summarized in Table 58. Only P and soils showed highly significant effects on the characteristics measured. Lime, as expected, had a highly significant effect on pH increase; the interaction $CaCO_3$xP had no significant effect on these parameters. There were no differences in PZNC among soils.

Prediction equations for the variables pH, ψo, (Gouy-Chapman potential), EC, and DM were obtained (Table 59). These equations were calculated by treating the variables as continuous to fit a response surface. The data showed that the linear and quadratic effects of P were significant for all the soils and variables measured, except on the pH of Guanipa 1 and El Potrero soils. These equations can be used to define a new experimental region using treatment combinations to determine increase in CEC without increasing EC to high levels.

For the three soils selected in this experiment, the highest dry matter yields were obtained with different treatment combinations. The highest dry matter yield and the least change in CEC after cropping were found in treatment combinations 43, 22, and 33 for Guanipa 1, Guanipa 5, and El Potrero, respectively.

Table 58. Effect of soil, $CaCO_3$, P, and interaction $CaCO_3$xP on the variables measured.

Variable	Soil	$CaCO_3$	P	$CaCO_3$xP
pH	**	**	**	NS
PZNC	NS	NS	**	NS
ψ_o	**	NS	**	NS
CM	**	NS	**	NS
EC	**	NS	**	NS
CEC	**	NS	**	NS

Table 59. Prediction equation for pH, ψo, DM, and CEC to fit a surface response for the three soils selected.

Soil Guanipa 5A															
pH	=	5.97	+	0.35	Ca**	-	1.16	P	**	- 1.06	Ca^{2**}	+ 0.31	P^{2**}
ψo	=	0.083	+	0.027	Ca**	-	0.017	P	*	- 0.005	Ca^{2**}	+ 0.007	P^{2**}
DM	=	-3.87	+	-.198	Ca	+	6.53	P	**	+ 0.041	Ca^{2}	- 1.36	P^{2**}
CEC	=	1.61	+	1.805	Ca*	-	0.103	P	*	- 0.345	Ca^{2*}	+ 0.631	P^{2**}
Soil Guanipa 1															
pH	=	4.97	+	0.380	Ca**	+	0.137	P		- 0.082	Ca^{2**}	+ 0.011	P^{2}
ψo	=	0.047	+	0.029	Ca*	+	0.0366	P	**	- 0.006	Ca^{2*}	- 0.004	P^{2*}
DM	=	-1.444	-	0.469	Ca	+	3.560	P	**	+ 0.102	Ca^{2}	- 0.582	P^{2**}
CEC	=	-0.819	+	1.830	Ca*	+	2.244	P	*	- 0.404	Ca^{2*}	- 0.256	P^{2}
Soil El Potrero															
pH	=	3.88	-	0.005	Ca**	+	0.394	P	**	+ 0.08	Ca^{2**}	- 0.033	P^{2}
ψo	=	0.016	-	0.013	Ca**	+	0.059	P	**	+ 0.004	Ca^{2*}	- 0.008	P^{2**}
DM	=	4.93	+	1.088	Ca**	+	5.077	P	**	- 0.166	Ca^{2**}	- 0.855	P^{2**}
CEC	=	-8.74	-	29.94	Ca	+	56.58	P	*	+ 7.944	Ca^{2*}	- 6.46	P^{2*}

*Significant.

**Highly significant.

SUMMARY AND CONCLUSIONS

Ten soils from Venezuela and one from Florida, U.S.A., were investigated by chemical, physical, and mineralogical techniques to elucidate surface reactivity. Also, three of the 10 Venezuelan soils were selected to determine the effect of lime and P levels on the surface charge. A sorghum crop was planted under greenhouse conditions to investigate the change of surface charge after cropping for each $CaCO_3$ and P treatment. Stern and Gouy-Chapman models for diffuse double layer together with the PZNC and the surface area were used to calculate the charge distribution and the CEC of the soils for each $CaCO_3$ and P treatment.

The following parameters were determined: (a) acidity sources; (b) quantity-intensity K parameters; (c) P fractionation in virgin soils and after P adsorption; (d) P adsorption isotherms at different temperatures and with different ionic systems; (e) PZNC of virgin soils and after $CaCO_3$ and P treatments; (f) pH before and after cropping; (g) electrical conductivity before cropping; and (h) dry matter yields.

The following parameters were calculated: (a) thermodynamic parameters associated with the adsorption process ($\Delta G°$, $\Delta H°$, $\Delta S°$) and (b) charge distribution in double layer, and CEC after $CaCO_3$ and P treatments.

Acidity measurements showed that exchangeable Al^{+3} and dissociation of OH groups from organic matter and silicates were responsible for the release of protons in these soils. The results of the Q/I technique and Gapon's equation indicated that the soils had a high selectivity for K

and low available K. Increasing temperature increased P adsorption in all soils. Study of ionic systems showed that some soils had a specific effect of $CaCO_3$ on P adsorption. Fractionation of soil P indicated that there was an increase of Al-P and Fe-P with temperature and quantity of P applied. Phosphorus decreased PZNC while P and $CaCO_3$ increased CEC through decreased PZNC and increased pH. Large applications of P and $CaCO_3$ resulted in electrical conductivity that may have depressed dry matter yields of sorghum. Calculations of thermodynamic paramters showed negative $\Delta G°$ values and positive values of $\Delta H°$ and $\Delta S°$.

From these results, it can be concluded that (1) exchangeable Al^{+3} and OH dissociation are the sources of acidity in these soils; (2) temperature increased P adsorption in all soils; (3) incubation temperature increase Al-P and Fe-P; (4) in some soils $CaCO_3$ had a specific effect on P adsorption; (5) P adsorption was a spontaneous endothermic reaction with an increase of entropy due to displacement of water molecules from the surface of phosphate ions; (6) the combined effect of increasing pH with lime and decreasing PZNC with applied P increased CEC; (7) the "new" CEC was not permanent but changed with cropping probably due to uptake of P and Ca by plants; (8) to obtain high yields of dry matter, the maximum increase in CEC must be sacrified; and (9) intermediate levels of $CaCO_3$ and P should be applied to these soils.

APPENDIX I

DETAILED CALCULATIONS FOR $CaCO_3$ AND PHOSPHORUS TREATMENTS

$CaCO_3$

From 1N KCl-exchangeable Al (Table 4),

El Potrero soil contained 3.020 meq Al/100g, then

100g : 3.020 meq Al as

1kg : x, and

x = 30.20 meq Al

1 meq of $CaCO_3$ will neutralize 1 meq of Al

30.20 meq $CaCO_3$ are needed to neutralize the exchangeable Al in 1kg of soil, so

30.20 meq x 50 mg of $CaCO_3$/meq = 1.51g

1kg of soil needs 1.51g $CaCO_3$ to neutralize the exchangeable Al.

Levels of $CaCO_3$ for 1kg of El Potrero soil are

0 Al^{+3} = 0g $CaCO_3$

1/2 Al^{+3} = 0.755g $CaCO_3$

1 Al^{+3} = 1.51g $CaCO_3$

2 Al^{+3} = 3.02g $CaCO_3$.

Phosphorus

To find parameters for the linear form of the Langmuir equation, data from Fig. 6 were used. The Langmuir equation is written as follows:

$$\frac{c}{x/m} = \frac{1}{Kb} + \frac{c}{b} \qquad (1)$$

The regression equation can be written as

where $y = a + bx$

$$y = \frac{c}{x/m}\ ,\ a = \frac{1}{Kb}\ ,\ \text{and}\ m = \frac{1}{b}\ .$$

The computer regression analysis when no supporting electrolyte was used showed values for San Cristóbal soil as follows:

$$y = 0.65 + 0.004x$$

$$\text{then}\quad b = \frac{1}{0.004} = 250 \text{ mg of P/100g soil} =$$

2,500 ppm P.

These levels were

0b = 0 ppm P

1/4b = 625 ppm P

1/2b = 1,250 ppm P

1b = 2,500 ppm P

from KH_2PO_4 (22.77% P)

$$\frac{b}{4} = \frac{2,500}{4} = 625 \text{ ppm P} = \frac{625 \text{ mg P}}{1 \text{ kg soil}} = \frac{2744.8 \text{ mg } KH_2PO_4}{1 \text{ kg soil}}$$

0b = 0g of KH_2PO_4

1/4b = 2.7g of KH_2PO_4

1/2b = 5.590g of KH_2PO_4

1b = 11.180g of KH_2PO_4

The same calculations were made for each soil.

APPENDIX II

DETAILED CALCULATIONS OF THERMODYNAMIC PARAMETERS BY THE METHOD OF BIGGAR AND CHEUNG (1973)

The data of P adsorption on Guanipa I soil at three temperatures are employed here to illustrate the detailed calculations:

Equation:

$$Cs = \frac{(\rho_1/M_1)A_1}{\frac{S}{Na(x/m)} - \frac{A_2}{M_2 \times 10^6}} \qquad (5)$$

was used to calculate the amount of solute adsorbed per milliliter of solvent in contact with the adsorbent surface (Cs). To calculate Cs, the cross sectional areas of the solvent (A_1) and the solute (A_2) are required and can be calculated by equation:

$$A = 1.091 \times 10^{-16}\left[\frac{M \times 10^{24}}{Na\rho}\right]^{2/3}. \qquad (6)$$

The cross-sectional area of the solvent (in this case, water) was calculated by putting the value M, Na, and ρ_1 in the above equation.

$$A = 1.091 \times 10^{-16}\left[\frac{18 \times 10^{24}}{6.02 \times 10^{23} \times 1}\right]^{2/3}.$$

$$A = 1.091 \times 10^{-16}\ (29.90)^{0.667}$$

$$A = 10.522 \times 10^{-16}\ cm^2/molecule.$$

The cross-sectional area of the solute molecule (in this case, KH_2PO_4) can be calculated similarly as follows:

$$A = 1.091 \times 10^{-16}\left[\frac{136.13 \times 10^{24}}{6.02 \times 10^{23} \times .2338}\right]^{2/3}$$

$$A = 1.091 \times 10^{-16}\ (96.55)^{.667}$$

$$A = 22.92 \times 10^{-16}\ cm^2/molecule.$$

Using:

ρ_1 = 1 g/ml

ρ_2 = 2.338 g/ml

M_1 = 18 g/mole

M_2 = 136.13 g/mole

S = 270 cm^2/g

Na = 6.02 x 10^{23}

and the following computer program:

```
DATA TODOS;
INPUT PA 1-5 1 PSN 6-9 1 SA2 10-12 1 SOIL
13-14 TEMP 15-16;
PAD = PA - PSN
PADS = PAD/(SA*100);
Cs = 3519.024*PADS;
YI = Cs/PSN;
YI = IN (YI);
PROC SORT; BY SOIL TEMP;
PROC GLM; BY SOIL TEMP;
MODEL LYI = Cs;
```

Where:

PA = P concentration of solution added in µg/ml

Ce = PSN = concentration of P at equilibrium in µg/ml

SA = survace area $m^2/100g$

PAD = x/m = P adsorbed µg/g

The print out gave the intercept for each soil and temperature, and that is the thermodynamic constant K for each temperature.

The free energy change was calculated by equation (9)

$\Delta G^\circ = -RT \ln Ko$

$\Delta G_5^\circ = 1.987 \times 278 \ln 1.17$

$\Delta G_5^\circ = 552.39 \times 0.16$

$\Delta G_5^\circ = -86.73$ cal/mole

$\Delta G_5^\circ = -0.09$ Kcal/mole

Enthalpy (ΔH°) was calculated by equation (10)

$$\Delta H^\circ = -R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{K_2}{K_1}$$

$$\Delta H^\circ = -1.987 \frac{278 \times 313}{278 - 313} \ln \frac{1.54}{1.17}$$

$\Delta H^\circ = -1.987 (-2486.1) \ln 1.30$

$\Delta H^\circ = 4939.91 \times 0.25$

$\Delta H^\circ = 1240$ cal/mole

$\Delta H^\circ = 1.24$ Kcal/mole

The entropy change (ΔS°) was calculated by equation (11) as:

$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$

$$\Delta S_5^\circ = \frac{(1240 \text{ cal/mole} - (-90 \text{ cal/mole})}{278}$$

$$\Delta S_5^\circ = \frac{1330}{278} = 4.78 \text{ cal/mole Ko}$$

The other methods used to calculate ΔG° are less reliable so the same equations were used; the difference is the K used and the limitation of its values.

APPENDIX III

DETAILED CALCULATIONS OF SURFACE CHARGE

The distribution of charge was calculated using the procedure proposed by Van Raij and Peech (1972) and using the following computer program.

```
DATA POST;
INPUT SOIL 1-2 Ca 3 P 4 pH 5-7 2 ZPC 8-10 2 PO 11-15 5 DM 16-18 2
REP 19 TRT 3-4;
IF SOIL = 1 THEN SA = 2.9;
IF SOIL = 2 THEN SA = 2.7;
IF SOIL = 3 THEN SA = 69.9;
N1 = 1E + 15;
Z = 1;
E = 1.6E-19;
Na = 6.02E + 23;
MN = 18;
RO = 1;
D = 89E - 12;
K = 1.38E - 23;
T = 298;
ED = 6E - 9;
PI = 3.1416;
GA = .9E - 8;
N = 30.1E + 19;
F = (Z*E*PO)/(2*K*T);
CONS = (2*D*K*T/PI)**.5;
```

```
SIGMA = CONS*N**.5*SINH(F);
PDIF = 4*PI*GA*SIGMA/ED;
PDEL = PO - PDIF;
F1 = (Z*E*PDEL)/(2*K*T);
SIGMA 2 = CONS*N**.5*SINH (1);
RAT = (NA*RO)/(MN*N );
MI = -2*F1;
SF1 = SINH(F1);
SIGMA 1 = (N1*Z*E)/(1 + RAT*EXP(MI);
EXPMI = EXP (MI);
CHARGE = SIGMA 1 + SIGMA 2;
CEC = CHARGE * 10360*SA;
SIGMA I = SIGMA 1*10360*SA;
SIGMA O = SIGMA 2*10360*SA;
SIGMA GC = SIGMA*10360*SA;
PZNC = ZPC;
PROC SORT; BY SOIL TRT;
PROC MEANS; BY SOIL TRT;
VAR SIGMA I SIGMA O SIGMA GC;
OUTPUT OUT=AVG MEAN=SIGMA I SIGMA O SIGMA GC;
```

Where:

Po = ψo

Soil 1 = Guanipa 5

Soil 2 = Guanipa 1

Soil 3 = El Potrero

ε = e

Na = Na

Mn = Molecular weight of solvent

Ro = ρ

D = ε

K = Boltzman constant

ED = ε^1 = average dielectric constant (=6)

ρI = π

GA = δ = thickness of double layer (0.9 R)

N = concentration number of ion/cm^3

PDEC = $\psi\delta$

Sigma I = inner layer charge

Sigma O = Stern layer charge

Sigma GC = Gouy-Chapman

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Melitón José Adams-Melendez was born 29 February 1944, at Urucure, Lara State, Venezuela. He graduated from Liceo "Pedro Emio Coll" in July 1963. In March 1964, he entered Universidad Central de Venezuela to pursue an Ingeniero Agrónomo degree, which he received in September 1970, with an orientation in Soil Science. As a student, he aided in teaching basic soil science courses while conducting research in plant physiology. In August 1971, he became an instructor at Universidad Central de Venezuela and was promoted to assistant professor in September 1973. He entered the University of Florida Graduate School in June 1974, and received the Master of Science degree in agriculture with a major in Soil Science in March 1976. In December 1976, he returned to Venezuela under a special research program. In September 1977, he was promoted to aggregate professor in the Universidad Central de Venezuela. He now is a candidate for the Doctor of Philosophy degree in soil science at the University of Florida.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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